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STUDIES ON ZINC RECOVERY FROM ZAWAR ANCIENT SLAG

By

RAKESH KUMAR

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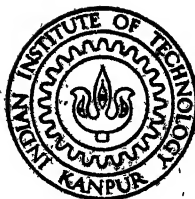
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DEPARTMENT OF METALLURGICAL ENGINEERING

INDIAN INSTITUTE OF TECHNOLOGY KANPUR

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STUDIES ON ZINC RECOVERY FROM ZAWAR ANCIENT SLAG

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By
RAKESH KUMAR

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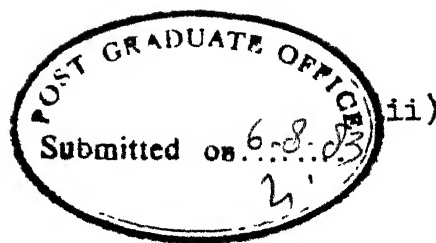
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CERTIFICATE

Certified that the present work entitled, "STUDIES ON ZINC RECOVERY FROM ZAWAR ANCIENT SLAG" by Rakesh Kumar has been carried out under my supervision and has not been submitted else where for the award of a degree.

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ABSTRACT

This work pertains to phase characterisation and recovery of zinc from Zawar ancient slag. Specific zinc-containing phases such as, hydrozincite, hemimorphite and willemite ~~etc.~~ have been identified. Various processing techniques show that the first non-silicate mineral can be easily leached by acid.

The second and third silicate minerals can also be leached by hot acid. However zinc recovery is apparently poor; this phenomenon has been ascribed to chelation or adsorption of Zn^{++} by colloidal/polymeric silicic acid. Neutralisation and coagulation of silicic acid by alum distinctly improve zinc recovery. 'Fast Leaching' techniques shows distinct promise. Above 80% recovery of zinc is reported.

CHAPTER I

INTRODUCTION

Technological developments in the extraction of zinc from materials like silicate ore, tails, leach residues and slags, which were considered as waste, have emerged out of realisation that "waste is no more waste". In order to conserve natural resources, people have been working in this direction since last fifty years or so.

Large heaps of ancient slags have been found in Zawar areas, Rajasthan. Availability of these slags in Zawar area bears testimony to an ancient smelting industry of impressive magnitude even though there are only fragmentary and inadequate account of this industry in written records (1). Based on field evidence and chemical analysis, it has been conjectured that 'slags' are product of the smelting of lead ore, but the smelting procedure, kind of flux and type of furnaces used are not known. The slags which are glassy to finely crystalline, contains 2-3 pct. Zn, 6-9 pct. Fe and traces of Pb and S. The quantity of slags present in Zawar areas has been estimated to vary between 30480 to 35560 tonnes (1). Thus the amount of zinc contained in it works out to be of the order of 900 tonnes.

1.1 Characterization of Ancient Slag:

A typical slag sample contains 2-3 pct. Zn, 6-9 pct. Fe, 0.1 - 0.5 pct. S, 22-30 pct. free silica (30-40 pct. total silica), 8-10 pct. Al, 4-6% Mg and traces of Cd, and Mn (Reported Superintendence Co., Calcutta).

Mineralogical characterisation of ancient slags has been carried out by Gangopadhyaya (2). He has established that slags are glassy material with some crystal inside. Various phases present in slag are: Hydrated zinc sulfate, $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$, sphalerite, ZnS ; Hemimorphite, $\text{Zn}_4(\text{OH})_2 \cdot \text{Si}_2\text{O}_7 \cdot \text{H}_2\text{O}$; Hydrozincite, $\text{Zn}_5(\text{CO}_3)_2 \cdot (\text{OH})_6$ and quartz SiO_2 .

Apart from the above phases, we have also observed some willemite Zn_2SiO_4 and calcium lead zinc silicate $\text{Ca}_2\text{ZnSi}_2\text{O}_7$ peaks in X-ray analysis. But their presence could not be verified by other techniques.

Chemical analysis of hot water leached sample showed carbonate ion but negligible trace of sulfate ion. The elements associated with zinc in the zinc bearing grains as detected by X-microanalysis are Zn, Al, Si and little Mg, Fe, Ca, Mn, K, Pb/S and Cu. Presence of little or nil Ca, and sulfur indicates that ZnS , Ca, Pb silicates are the phases which are less likely to be present. The size of the Zn bearing grain lies between $0.5\mu - 8\mu$. In the X-ray microanalysis of some individual particles of slags, there were some particles which contained only one element i.e. Si, indicating there are pure phases like silica. In some particles, X-ray microanalysis at different areas of single particle indicated presence of large number of

element like Mg, Mn, Fe, Ca, Pb/S, K, Al, Si but no Zn. But all the zinc containing areas of a particle contained all other elements like Mg, Mn, Fe, K, Ca, Pb/S, Al and Si. Out of eight particles only one contained zinc which indicated that zinc is segregated in the sample (2).

Quantification of various phases present has not been done. But silicate, zinc hydroxycarbonates and free silica seem to be the major phases present as supported by various evidence mentioned above (2).

1.2 Literature Review:

Materials like zinc silicate ore, ancient slags, retort content and lead blast furnace slags may be put in one category, i.e. siliceous material, due to identical phases present in them. Literature pertaining to zinc extraction from these materials may be reviewed together. The various zinc phases present in these materials are smithsonite (ZnCO_3), hydrozincite ($\text{Zn}_5(\text{CO}_3)_2 \cdot (\text{OH})_6$), hemimorphite ($\text{Zn}_4(\text{OH})_2\text{Si}_2\text{O}_7 \cdot \text{H}_2\text{O}$), willemite (Zn_2SiO_4), zinc ferrite ($\text{ZnO} \cdot \text{Fe}_2\text{O}_3$) and other complex silicate of Zn with Pb, Ca and Al. There are large numbers of pyrometallurgical and hydrometallurgical techniques applied to recover zinc from these materials. Various pyrometallurgical techniques include slag fuming, chlorination, and high temperature sulfation. Both acid and Alkali leaching have been tried with certain modification. The suitability of a particular treatment for a particular material is determined by zinc phases

present, composition, nature of gangue minerals, cost and ecological factors.

1.2A Pyrometallurgical Processes:

Zinc fuming processes are used commercially both for lead blast furnace slag and silicate ores. Theoretical and industrial aspects of these processes have been studied most thoroughly (3,4,5,6,7). The process is based on high temperature (1100 - 1300°C) reduction with C, CO and H₂ in a shaft type or kiln type furnace. Most of the slags treated contain zinc ranging from 10-20% and zinc recovery is of the order of 80-85% i.e. 2-3% zinc remains unrecovered. The process has been found quite promising when the raw materials contain phases like zinc ferrite (difficult to leach) or large amount of carbonaceous gangue (increases acid consumption).

Chlorination has been tried experimentally^{or} upto pilot plant level. Chlorination with Cl₂ gas or Cl₂-CO/Cl₂-O₂, gas mixture (8-12) and chlorination with salt like FeCl₃, CaCl₂ and NaCl-AlF₃ (13,14) have been experimented recently and good recoveries of Zn have been reported. However, chlorination has not been used on industrial scale due to certain problems such as design of leaching vessel etc. Apart from zinc fuming and chlorination, other experimental ideas includes vacuum sublimation of zinc* directly from slag at temperature 1200-1300°C and pressure, 0.1 mmHg (15),

* as zinc vapour

high temperature (600-1000°C) sulfation with FeSO_4 (salt) SO_2 , SO_3 (gases) (16) and sulfuric acid (17).

1.2B Hydrometallurgical Processes:

Both acid and alkali medium leaching have been tried for recovering zinc from siliceous materials. Acid leaching has been carried out mainly with sulfuric acid, using some modification in conventional leaching. Different alkali tried, are caustic soda (NaOH) Ammonia-Ammonium carbonate ($\text{NH}_3 - (\text{NH}_4)_2\text{CO}_3$) and sodium cyanide (NaCN). Mathew and Elsner (18) have reviewed the hydrometallurgical treatments of zinc recovery from silicate ores.

Sulfuric acid leaching of zinc silicate phases result in the formation of monomeric and dimeric silicic acid along with zinc sulfate. These silicic acid polymerizes with time and attains colloidal dimensions. It is believed (19,20,21,24,30) that interaction of zinc ions with colloidal silica at low pH, and subsequent occlusion on precipitation result in low recovery of zinc. Zinc may be adsorbed/occluded in free silica, silicic acid, i.e. monomers or polymers etc. Amount of zinc occluded may be a complex function of the proportion of all the above phases and hence may depend upon the purity of solid sample. Apart from the above mentioned problem, other factors like presence of large amount of carbonaceous gangue and unselective dissolution of minerals often makes the use sulfuric acid leaching questionable.

Various approaches used to tackle the colloidal silica problem includes.

(I) Alternative methods, e.g., leaching with Alkali and chlorination etc.

(II) Modification in conventional sulfuric acid leaching, i.e., handling of colloidal silica problem: (a) Chemically e.g. by adjusting parameters like pH, temperature, time and addition of polyvalent metal ions such as Al^{3+} , (b) Thermally affecting the precipitation of silica in crystalline form.

In alkali-leaching, all the problems encountered in sulfuric acid leaching are solved, i.e. no colloidal silica formation, selective dissolution, carbonate gangue can be handled. Various Alkali used are NaOH (21,22,23) NaCN (24,25,26) and $NH_3-(NH_3)_2CO_3$ (27). Alkali leaching has not been tried beyond pilot plant level because of large reagent consumption (4-5 times more than stoichiometric), and problems in Zn recovery from leach solution. For example in NaCN leaching, to keep the zinc in solution NaCN/Zn ratio should be 4/1 and for its cathodic deposition, it should be the other way round (22).

Silicic acid problem has been handled chemically, either by adjusting parameters like pH, temperature and addition of polyvalent ions, or by controlling the nature of zinc silicate-sulfuric acid reaction in a water starved system (discussed later).

For the first case effect of various parameters on nature of silicic acid in solution may be mentioned briefly. Soluble monosilicic acid which is quite stable at pH 2 or less (28,30), and concentration less than 100-200 ppm (as silica) (29), can be precipitated in easily filterable crystalline form if pH is raised to 4-5 (30,19). With increasing time, temperature and pH (especially above 7), polymerization of monosilicic acid is enhanced (28,19). Polymerized silicic acid can be precipitated only in the form of difficulty filterable gelatinous precipitate in which all or much of the zinc is occluded/adsorbed (19,20,28). The unique position of Al^{+++} ions with respect to silicic acid and silica is well known. Al^{3+} ions play a dual role; (i) it decreases the solubility of silica (31); (ii) colloidal silica can be precipitated most effectively in pH range 4-5. This is because below pH 4, the charge on silica is too small and above pH 5, charge is quite large so large amount of Al^{+++} ions is required. Al^{+++} ion combines with soluble silica in pH range 5-9 (31,32).

Electrolytic Zinc Company of Australia and integrated pilot plant at Palmerton are successfully extracting zinc from zinc silicate ore by controlling factors like pH, time and temperature in sulfuric acid leaching (19,33,30). Radino process (Brazil) is using Al^{+++} ions in addition to the control of above factors (20,34).

Montagne process (multistage) (35) and process described in Canadian Patent (single stage) (36) leaching is carried out in such a way that silicic acid is precipitated in crystalline form controlling the concentration of silicic acid ^{to} less than 100 ppm in a stage.

Fast leaching (12) also referred as Quick leach (37) or Jowanda Process (36) is a process of leaching, where precipitation of silica is controlled chemically, taking advantage of water starved nature of silicate minerals in concentrated acid (37). Water starved nature result in rejection of silica in crystalline form and not in the form of silicic acid. This process has been tested for twelve different types of silicate minerals. Non-selective leaching and large acid consumption are the only problems with this process.

Pug Roasting i.e. heating of slag and sulfuric acid mixture below the boiling point of sulfuric acid (12) and Auto clave leaching (Italish Process) of slag (39) are examples where precipitation of silica in crystalline form is controlled thermally.

Hydrochloric acid leaching of Outkumpu slag (40) and Auto clave leaching of ore containing SiO_2 using NaOH has also been reported (41).

Definition of the Problem:

The basic goal being to recover zinc from ancient slag, the work undertaken was firstly, to consider the different processing techniques and ~~the~~ study, the disappearance of difference phases and secondly, to concentrate on a few promising techniques such as sulphuric acid treatment.

CHAPTER II

MATERIALS AND EXPERIMENTAL TECHNIQUES

2.1 Materials:

The details of various raw materials and chemicals used in our investigation are given below:

(a) Ancient Slags: This was supplied by Hindustan Zinc Ltd., Udaipur. The total contents roughly 40 Kgs. were sieved through $1\frac{1}{2}$ ", 1" and $\frac{3}{4}$ " aperture meshes. The different fractions were separately cone-quartered. A quarter of each size fraction was taken and mixed. The total 10 Kg. material was crushed in Jaw Crusher and Rolls, till the entire product was -65 mesh. Small cone-quartered samples from -65 mesh material were used for further grinding to get the desired size for experimentation.

(b) Ore Samples Containing Hemimorphite and Willemite Minerals: These were supplied to us by Electrolytic Zinc Company of Australia. It was reported by them that samples containing willemite (Beltana Ore, South Australia) and hemimorphite sample contained 30 pct. and 45 pct. Zn respectively.

(c) Chemicals: All chemicals used were of analytical grade. The various chemical used are, sulfuric acid (H_2SO_4), Hydrochloric acid, (HCl), Nitric acid (HNO_3), Sodium Carbonate (anhydrous) (Na_2CO_3), Aluminum sulfate ($\text{Al}_2(\text{SO}_4)_3 \cdot 16\text{H}_2\text{O}$), Sodium Metasilicate ($\text{Na}_2\text{O} \cdot 2\text{SiO}_2$), Sodium hydroxide (NaOH),

Silica powder (SiO_2) and pure Zn metal.

2.2 Experimental Techniques:

(a) Estimation of Zinc: Zinc in leaching solution was analysed by conventional gravimetric method and atomic absorption spectrophotometry.

(i) Conventional Gravimetric Analysis: Zinc was estimated by group separation followed by precipitation to zinc sulfide and subsequent ignition to zinc oxide at 900°C .

(ii) Atomic Absorption Spectrophotometry: This is a suitable method of analysis by which zinc can be measured accurately at low concentrations. The significant details are provided in Appendix A.

(b) X-ray Analysis: X-ray diffraction studies on slag samples obtained after various treatments were carried out using GEC, XRD-6 Diffractometer. A small amount of powder slag sample was taken in a perspex specimen holder and mounted on the specimen stage of diffractometer. $\text{CuK}\alpha$ radiation with Ni filter was used and intensity versus 2θ plots were recorded on chart paper.

X-ray diffraction pattern after a particular treatment was compared with corresponding diffraction pattern of representative original slag sample. This was done to minimize complexities which arise due to wide heterogeneity in the slag and reflected in x-ray diffraction pattern. Criteria used for

comparison include:

- intensity of peak
 - number of times appearance of a peak
 - appearance and disappearance of peaks
- and
- expected behaviour of phases eg. hydrozincite, zinc sulfate heptahydrate, zinc sulfate etc.

The last criterion was used to partially simplify the problem of occurrence of large number of phases corresponding to a particular interplanar spacing value 'd', 'd' values were matched in error limit of $\pm 0.015 \text{ \AA}$.

(c) Chemical Leaching: The set up used for leaching is shown in Figure 1. Leaching was carried out in a four neck reaction kettle of 1L capacity. Water/oil bath was used for heating. Temperature of bath and hence reaction kettle was maintained using, Beckmann thermometer with a heater and controller. In case of water bath, temperature control was found to be difficult at higher temperature due to large evaporation loss, so oil bath was preferred for better temperature control. Stirrer, S_1 and S_2 coupled with variable speed motors were used for stirring the oil bath and pulp inside the reaction kettle.

All the leaching experiments were carried out at atmospheric pressure.

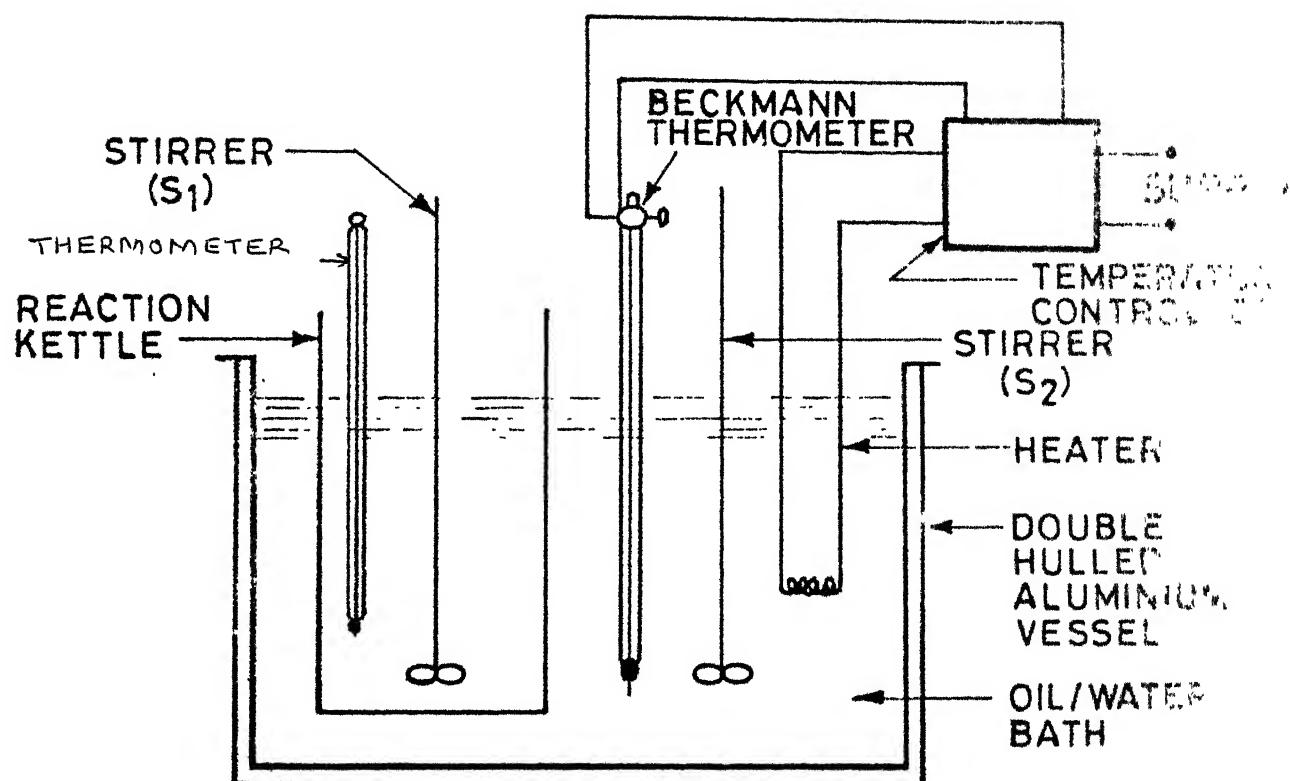


FIG.1. SCHEMATIC DIAGRAM OF LEACHING SET UP

CHAPTER III

DIFFERENT PROCESSING TECHNIQUES — PHASE STUDIES

These include heating of slag to different temperatures, with or without acid, and various chemical leaching experiments. The purpose has been to find out the response of slag to these treatments with respect to phase changes and zinc recovery.

3.1 Description of Treatments:

A. Acid Leaching: 2-2.5 Kg slag, ground to desired size was cone-quartered to sample size of 250-350 g, which was used in four to five leaching experiments. The corresponding 'twin' was retained for chemical and x-ray analysis. Leaching was carried out in a 1L leaching vessel at a suitable temperature $T \pm 5^{\circ}\text{C}$ (water bath temperature), initial pulp density p (%), acid concentration $X(\text{N})$, for 4.5-5.0 hrs, under moderately high stirring conditions. Filtration was done at room temperature. Leach residue was washed completely and analysed by x-ray diffraction technique. Filtered solution was retained for chemical analysis.

B. Other approaches - using H_2SO_4 , (Temp. 250°C): 1-1.5 Kg slag (-100 mesh) was cone-quartered to sample size of 150-175 g and used in the following treatments. Corresponding 'twin' was retained and analysed by x-ray and chemical analysis.

1. Sulfuric Acid Leaching in Presence of Aluminium Sulfate: This is referred to as Modified sulfuric acid leaching in further discussion. 50 g slag was leached with 2N- H_2SO_4 (500 ml) and 10 g of aluminium sulfate ($\text{Al}_2(\text{SO}_4)_3 \cdot 16\text{H}_2\text{O}$) at temperature $90 \pm 5^\circ\text{C}$ (water bath temperature) for 4 hrs in 1L leaching vessel under moderately high stirring conditions. Filtration was done in hot condition. Residue was washed completely with distilled water and analysed by X-ray diffraction technique. Filtered solution was retained for chemical analysis.

2. Fast Leaching: 50 g slag was mixed with sulfuric acid (sp.gr.1.84) and water in the ratio 1:1:1 by weight. Crumbled mass, thus obtained, was kept as such for 1 hr (Fast Leach) and then water leached at 90°C (water bath temperature) for 1.5 hrs. Filtration was done in hot condition. Residue was washed completely, dried and X-ray analysed. Filtered solution was chemically analysed for zinc.

3. Pug Roasting: Pug roasting is baking of a mixture of slag and concentrated sulfuric acid below boiling point of sulfuric acid i.e., 338°C . 50 g slag was mixed with concentrated sulfuric acid (sp. gr. 1.84) in the ratio 1:1, by weight, and baked at 200°C for 15 minutes. Resulting cake was treated in a manner similar to fast leaching.

G. Heating of Slag to High Temperatures: Approximately 1.0 Kg slag (-200 mesh) was cone-quartered to sample size of 50-60 g and used in the following experiments. Corresponding

'twin' was retained and analysed by X-ray.

1. Heating without Acid: 5-8 g of slag samples were heated to 700°C (below zinc ferrite formation temperature: 740°C) and 900°C (above zinc ferrite formation temperature). Samples were cooled to room temperature in air. Each sample was divided into two parts. One part from each sample was analysed by X-ray without any further treatment. The remaining part was leached with acid, washed and X-ray analysed. Leaching was carried out with 2N H_2SO_4 at room temperature ($\approx 35^\circ\text{C}$) for 48 hours.

2. Heating with Sulfuric Acid: Heating experiment similar to (1) were repeated by mixing slag with 20% (by weight sulfuric acid).

3.2 Experimental Data:

X-ray diffraction patterns for various samples before and after processing, are shown in Figure 2-8. Figure 2 shows the diffraction pattern of slag after leaching with sulfuric acid along with diffraction pattern of corresponding representative original slag sample. There is evidence of disappearance of some hydrozincite peaks and some increase in intensity of SiO_2 peak. Zinc silicate peak seems to remain unchanged.

There are large number of SiO_2 peaks appearing in diffraction patterns of leach residue after $(\text{H}_2\text{SO}_4 + \text{Al}_2(\text{SO}_4)_3)$ leaching (Figure 3) and residue after fast leaching (Figure 4), as compared to original slag sample. Increase in the intensity of existing silica peak is also remarkable in leached sample.

There is some disappearance of silicate peak, but most of them remain. Zinc sulfate peaks disappear in leached samples. Due to overlapping of phases for different 'd' values, it is difficult to comment on the disappearance of hydrozincite though it is expected to disappear.

X-ray diffraction pattern of pug-roasted and water leached sample (Figure 4), shows disappearance of large ^{numbers} ~~no~~ of zinc silicate, zinc sulfate and hydrozincite phases. The behaviour of SiO_2 peak is same as described earlier for residues after fast leaching and $(\text{H}_2\text{SO}_4 + \text{Al}_2(\text{SO}_4)_3)$ leaching.

Diffraction patterns of slag heated to 700°C and 900°C without acid, are shown in Figure 5 and Figure 6, before and after leaching. Disappearance of hydrozincite was marked in the heated samples in both the cases. Other peaks seem to remain unchanged. Appearance of zinc ferrite phase peaks was marked for sample heated at 900°C (above zinc ferrite formation temperature, 740°C). Peaks corresponding to zinc ferrite remain unaffected on leaching.

Diffraction pattern for slag heated to 700°C with H_2SO_4 (Figure 7), shows strong evidence of zinc sulfate, and zinc oxy-sulfate formation. This has been further supported by disappearance of these peaks in the diffraction pattern of sulfated and leached sample. Zinc ferrite formation has been marked in diffraction pattern (Figure 8) of slag sulfated at 900°C with H_2SO_4 . No new zinc sulfate peaks were observed in this case.

Diffraction patterns of original slag varied to some extent from one sample to another. In some samples, peaks corresponding to willemite or calcium lead zinc silicate were marked, which indicated their presence in slag. Possibly due to heterogeneous character of slag, their occurrence could not be marked in some original slag sample. Hemimorphite, willemite and calcium lead zinc silicate have been jointly referred to as zinc silicate phase in earlier description of Figure 2 to Figure 8.

Zn analysis of slag and filtered leach solutions were carried out by conventional wet chemical method. Reported values of recovery are approximate, because fluctuations were observed in zinc analysis of slag samples, especially for coarser sizes (e.g. - 100 mesh). An average value of Zn% for a particular representative sample was used for recovery calculations. Recovery values are expected to lie in the error limit $\pm 10\%$.

Table 1 shows result of slag leaching with different acids under identical conditions. Nitric acid shows the maximum recovery of 63%. Recovery is 31 and 50% for H_2SO_4 leaching in two different conditions.

Table 2 shows the result of other leaching techniques using H_2SO_4 . Maximum recovery of approximately 68% was obtained in the leaching of pug roast slag.

Various X-ray findings for different treatments have been summarized in Table 4 along with corresponding recovery values. For heating experiments recovery values could not be found out due to smallness of experiments. A list of symbols used in Figure 2 to Figure 8 and Table 4 is given in Table 3.

3.3 Discussion:

A review of the results indicate that hydrozincite is a relatively more leachable phase compared to zinc silicate phases such as hemimorphite. Stepwise increase of recovery in ordinary sulfuric acid leaching, fast leaching and pug roasting coupled with X-ray evidences, suggest that phases like hemimorphite, willemite and calcium lead zinc silicate may be made to disappear under more drastic conditions. Mathew and Elsner (19) on the other hand, point out that both hemimorphite and willemite are easily leachable with sulfuric acid.

Low recovery of zinc from zinc silicates by ordinary sulfuric acid leaching is usually explained (19,20,24,27,30) in terms of adsorption/occlusion of zinc in silicic acid (monomer and polymer) and colloidal silica.

It seems that, free silica in the ore/slag also plays an important role. As Iller (42) points out that residual valences of the siloxone ($-\text{Si}-\text{O}-\text{Si}-$) surface of silica react with water such that surface becomes covered with silanol (SiOH) group. The silica surface covered with $-\text{OH}$ group is expected to

behave in a manner similar to polysilicic acid. In a system like ours, where large % free silica exist in the slag, it might have important implication along with the earlier proposed theory.

Heating of slag at 700-900°C makes hydrozincite phase disappear, but there is appearance of zinc ferrite phases. Subsequent leaching does not show any disappearance of peak and hence zinc recovery may not be high. Recently Colussi et.al. (43,44) have reported that air heating of slag at temperature above 900°C, for a prolonged time (Imperial Smelting Process) result in complete oxidation of crustile phase (the only phase present in crystalline form in glassy matrix) to magnetite with simultaneous concentration of all zinc in a single phase : a solid solution between magnetite and franklinite, ZnFe_2O_3 . This solid solution is easily leachable as compared to zinc ferrite. Apart from zinc ferrite, there is appearance of magnetite when ancient slag is heated at 900°C, prolonged heating of ancient slag might yield similar result.

Heating of slag at 700°C with H_2SO_4 , prior to leaching, may give good result, since there is strong evidence of zinc sulfate, zinc oxy-sulfate formation, which are easily leachable. At 900°C, there is formation of zinc ferrite, which must be avoided. Similar observations were made by Akerkar et.al. (17), in sulfation of Chakula (Bhutan) complex silicate type ore, which contained hemimorphite. Zinc recovery decreases drastically when temperature of sulfation used by them exceeded 740°C.

Based on the above findings and literature survey, research efforts could be directed in the following areas:

1. Fast Leaching
2. Sulfuric Acid Leaching and Modified Sulfuric Acid Leaching
3. Pug Roasting
4. High Temperature ($< 740^{\circ}\text{C}$) Sulfation with Sulfuric Acid, ~~and~~ for which X-ray results are quite encouraging
5. Experiments similar to fast leach with HCl
6. Chlorination with salts or $\text{Cl}_2/\text{Cl}_2\text{-O}_2/\text{Cl}_2\text{-CO}$
7. Alkali leaching

However, for the chlorination route, the materials of construction pose a big problem in the present Indian condition. Hence chlorination route was not attempted.

Due to large reagent consumption, problem of recovering zinc from leach solution and lean nature of slag, alkali leaching was not tried. It may be noted that zinc % of slag could not be upgraded by beneficiation e.g. magnetic separation and flotation etc.

In the zinc smelter of Hindustan Zinc Ltd., sulfuric acid is a by-product which is available in large quantities. So in this work, research efforts have been focussed on ideas using sulfuric acid, mainly fast leaching, sulfuric acid leaching and modified sulfuric acid leaching. Time limit did not permit us to try other ideas, namely pug, roasting and high temperature sulfation.

TABLE 1

Leaching of Slag with Different Acids
 Vessel Capacity 1 lit. Pulp concentration, P 10%

Expt. No.	Experimental Conditions					Results		
	Acid	Concn. x(N)	Temp. T(°C)	Time (hrs.)	Size (mesh)	% Zn in slag	Zn leached (g/100 g slag)	Recovery (%)
1(a)	HCl	2	80	4.5-5.0	-200	2.87	1.22	42.5
1(b)1	H ₂ SO ₄	2	80	4.5-5.0	-200	2.87	0.90	31.0
1(b)2	H ₂ SO ₄	4	90	9.0-9.5	-400	2.79	1.29	51.0
1(c)	NH ₄ O ₃	2	80	4.5-5.0	-200	2.87	1.83	63.7
1(d)	Aqua- regia	2	80	4.5-5.0	-200	2.87	1.65	58.0

TABLE 2Results of other Leaching Techniques

Expt. No.	Description			
		% Zn in slag	Zn leached (g/100 g slag)	Recovery (%)
2	($\text{H}_2\text{SO}_4 + \text{Al}_2(\text{SO}_4)_3$) leaching	2.02	1.15	57
3	Fast Leach	2.02	1.10	55
4	Pug Roasting	2.02	1.35	67

TABLE 3List of Symbols Used in Fig.2 to 8 and Table 4

Phase	Symbol
Silica (SiO_2)	- -
Hemimorphite ($\text{Zn}_4(\text{OH})_2\text{Si}_2\text{O}_7 \cdot \text{H}_2\text{O}$)	HMR
Willemite (Zn_2SiO_4)	WLM
Zinc Sulfate (ZnSO_4)	ZS
Zinc Oxysulfate ($2\text{ZnO} \cdot 3\text{ZnSO}_4$)	ZSO
Zinc Sulfate Heptahydrate ($\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$)	ZSH
Hydrozincite ($\text{Zn}_5(\text{CO}_3)_2(\text{OH})_6$)	HZ
Calcium Lead Zinc Silicate ($\text{Ca}_3\text{Pb}(\text{ZnSiO}_4)_4$)	CALZS
Zinc Ferrite ($\text{ZnO} \cdot \text{Fe}_2\text{O}_3$)	ZFE

TABLE 4
Summary of Results

Expt. No.	Description	X-ray Results For Slag After Treatment		Approx. (%)
		Phase	Comment	
1	H ₂ SO ₄ Leaching	HZ, other Zn phases,	disappears, inconclusive,	30-50
2	(H ₂ SO ₄ +Al ₂ (SO ₄) ₃) Leaching	SiO ₂ , HMR,WLM/ CALZS,HZ, ZS/ZSH/ZSO,	increase in intensity, slightly affected, disappears, most of the peaks dis- appears,	57
3	Fast Leaching	Phase as above	Comments as above	55
4	Pug Roas Leaching	SiO ₂ , HMR/WLM/ CALZS,HZ, ZS/ZSH/ZSO	increase in intensity, large nos.of peaks disappear, disappears, disappear,	67
Slag Heated to 700°C, 2 hrs:				
5(a1)	Before Leaching	HZ, other phases	disappears, inconclusive	
5(a2)	Same, after Leaching Slag Heated to 900°C, 2 hrs.	All phases,	No apparent change,	-
5(b1)	Before Leaching	ZFE, HZ, other phases,	appears disappears, inconclusive,	-
5(b2)	After Leaching	Above phases,	No further change,	-

Contd.....

Table 4 (Continued):

Expt. No.	Description	X-ray Result for Slag After Treatment		Approx. Recovery (%)
		Phase	Comment	
	Sulfation at			
6(a1)	700°C, before Leaching	ZS/ZSO, HZ, other phases,	appear, disappears, inclusive	-
6(a2)	After Leaching	ZS/ZSO,	disappear,	-
6(b1)	900°C, before Leaching	ZFE, HZ, other phases	appears, disappears, inconclusive	-
6(b2)	After Leaching	Above phases,	inconclusive,	-

- means no zinc recovery analysis was done due to smallness of the sample.

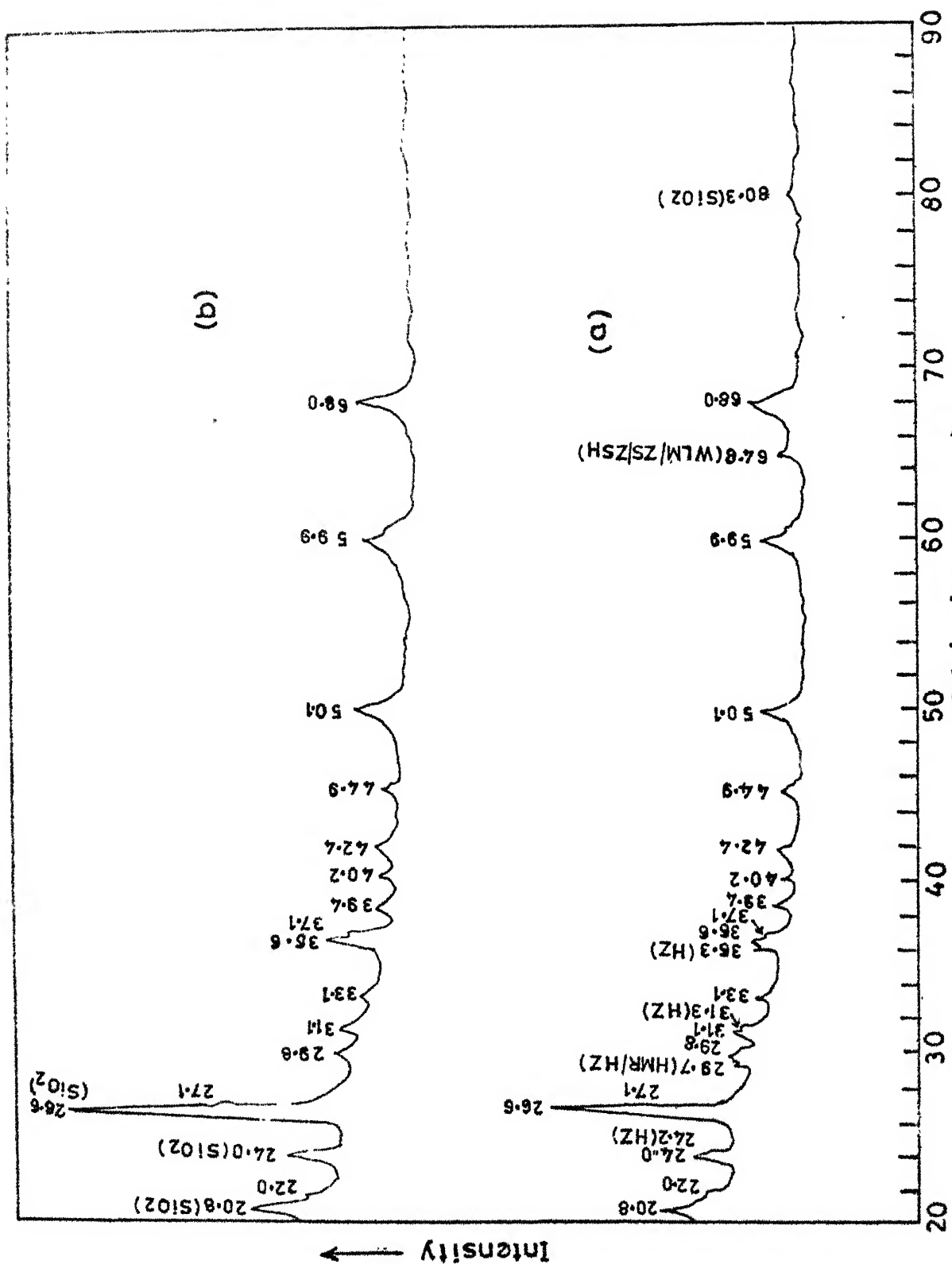


Fig. 2 : Comparison between (a) Original Slag Sample (b) Leach Residue after H_2SO_4 leaching.

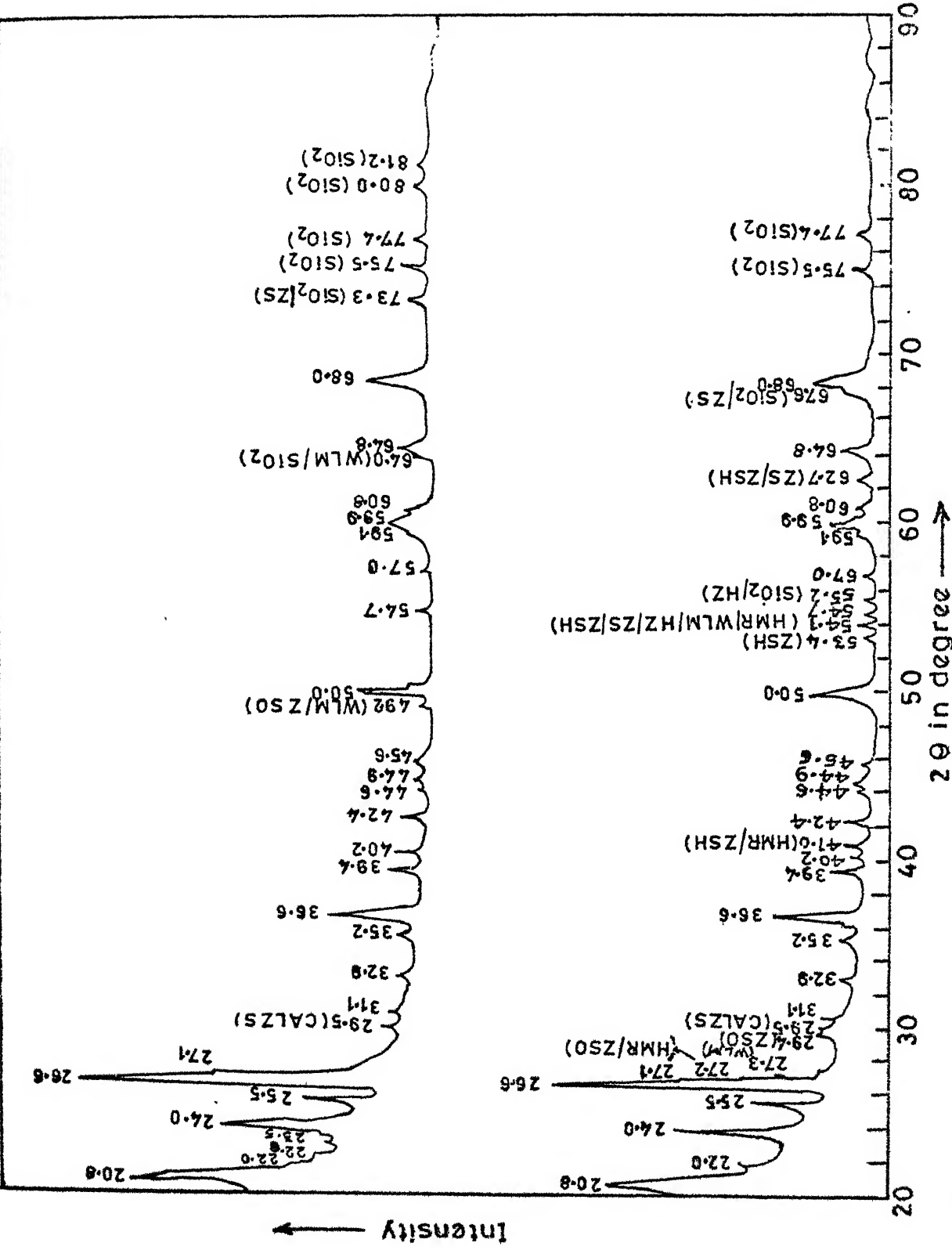


Fig. 3 Comparison between (a) Original Slag Sample (b) Leach Residue after $[Al_2(SO_4)_3 + H_2SO_4]$ leaching.

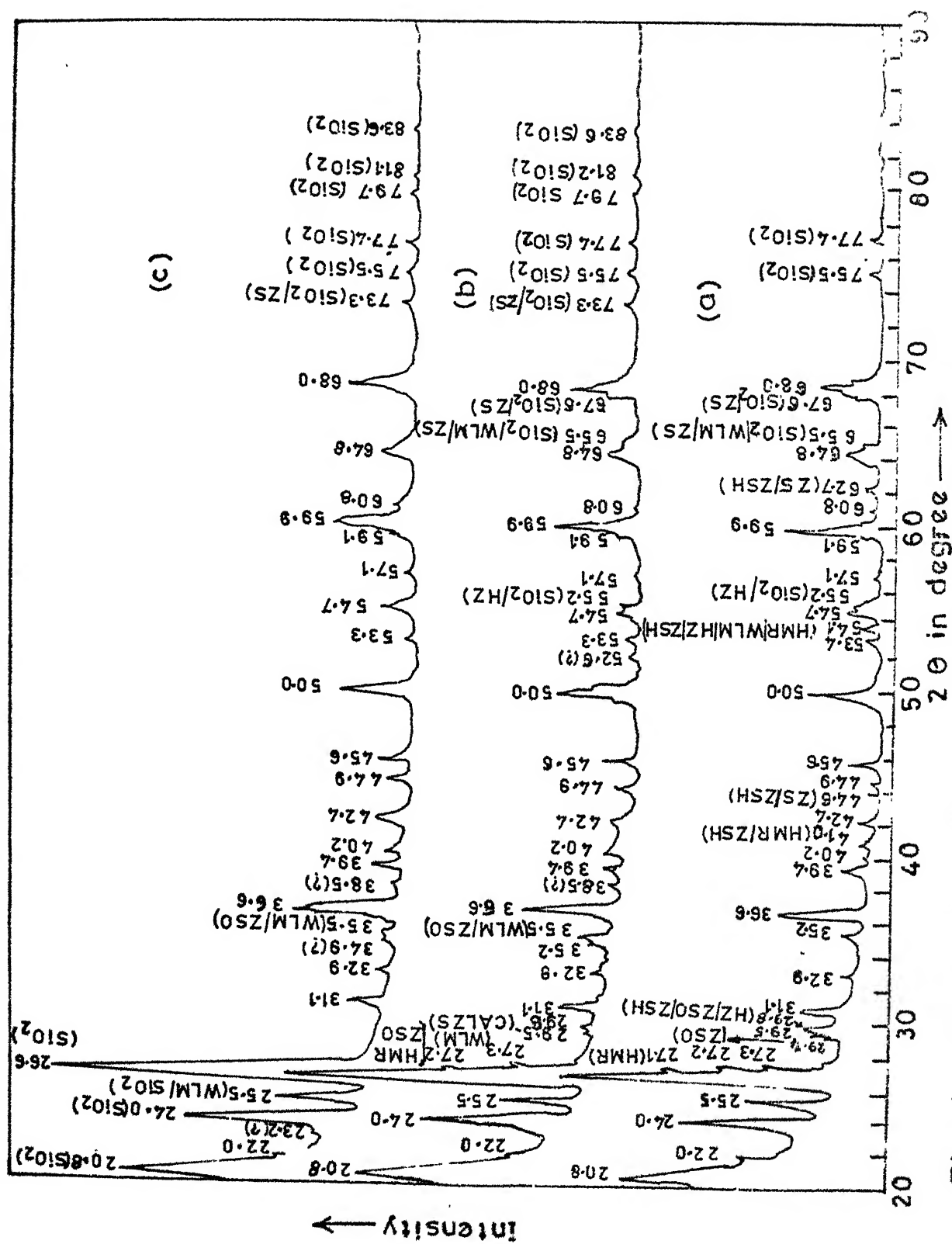


Fig. 4 . Comparison between (a) Original Slag Sample (b) Leach Residue after fast leaching and (c) Leach Residue after PugRoast leaching.

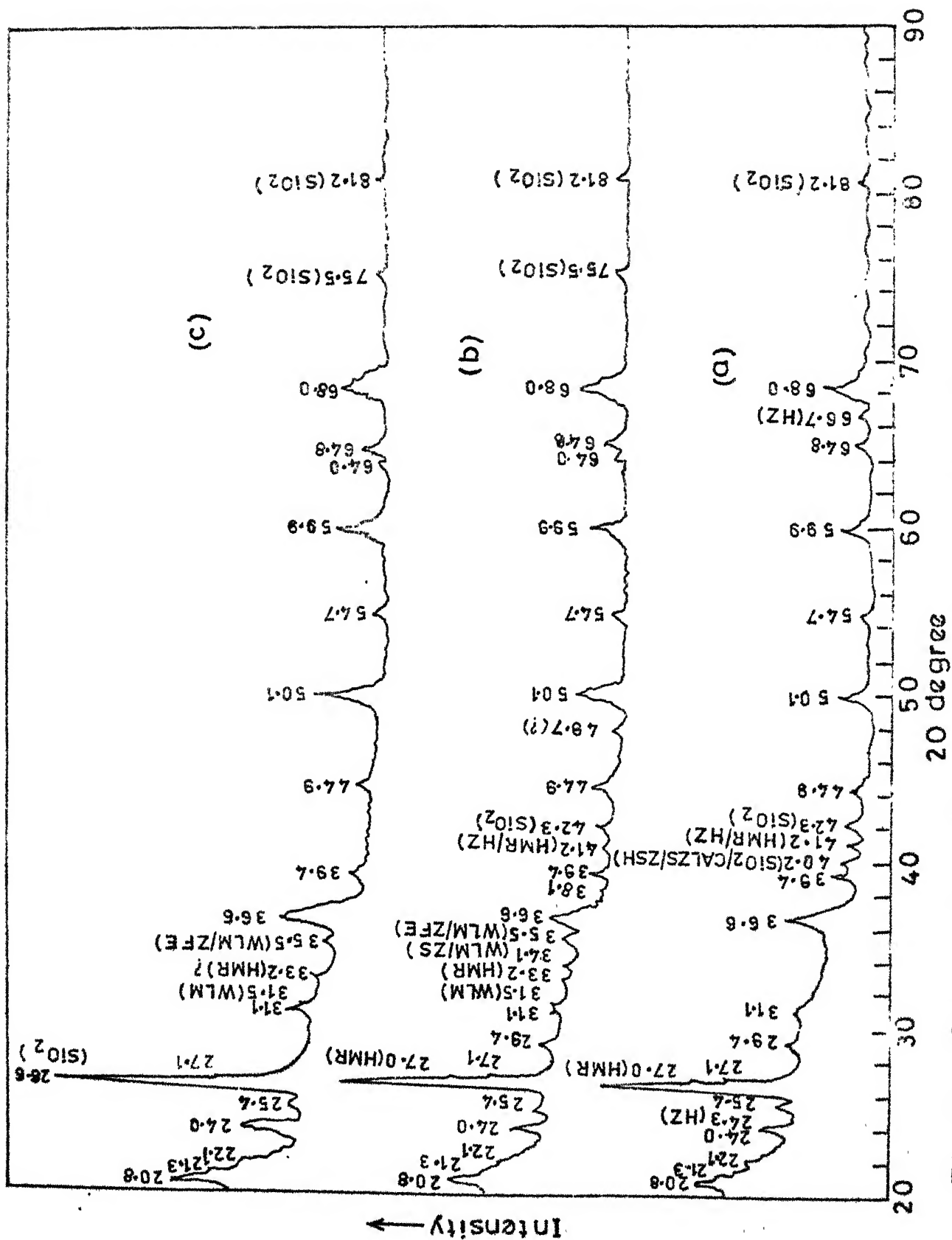


Fig. 5 . Comparison between (a) Original Slag Sample (b) Slag heated to 700°C, 2 hrs. (c) Slag heated and leached out with H₂SO₄ .

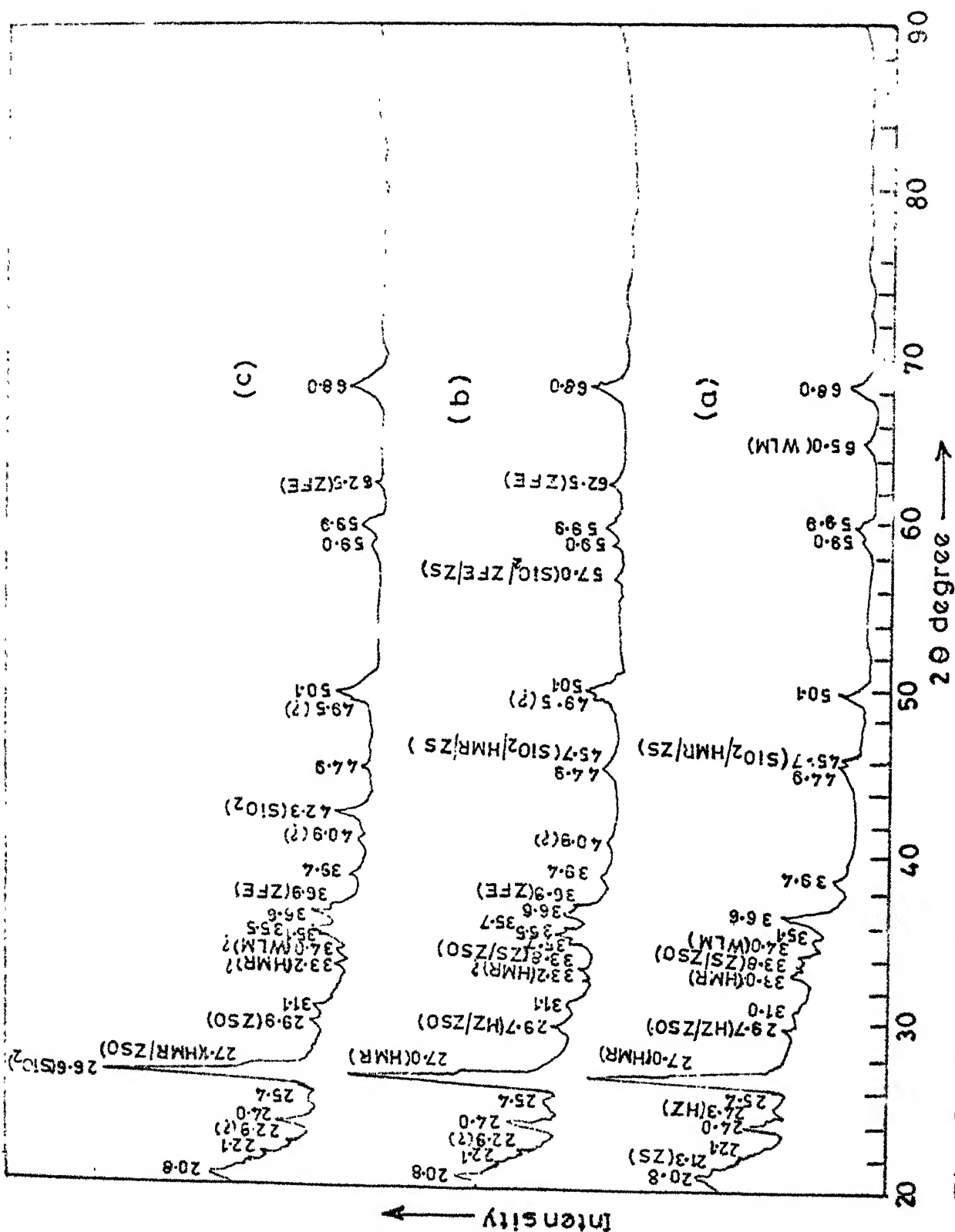


Fig. 6 . Comparison between (a) Original Slag Sample (b) Slag heated to 900°C, 2 hrs. (c) Slag heated and leached out with H_2SO_4 .

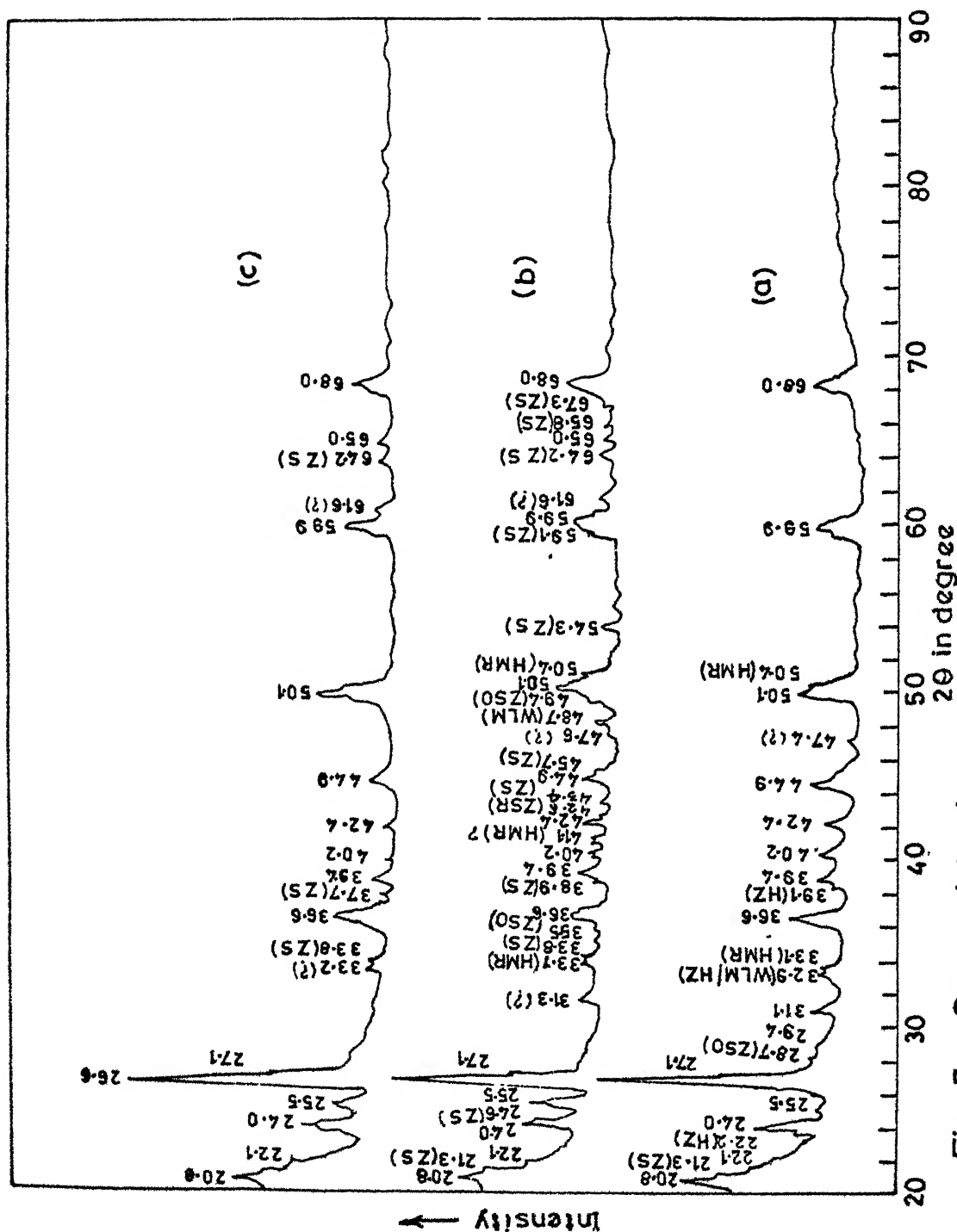


Fig. 7. Comparison between (a) Original Slag Sample (b) Sulfated with H₂SO₄ at 700°C, 2 hrs. (c) Residue after leaching of Sulfated Slag.

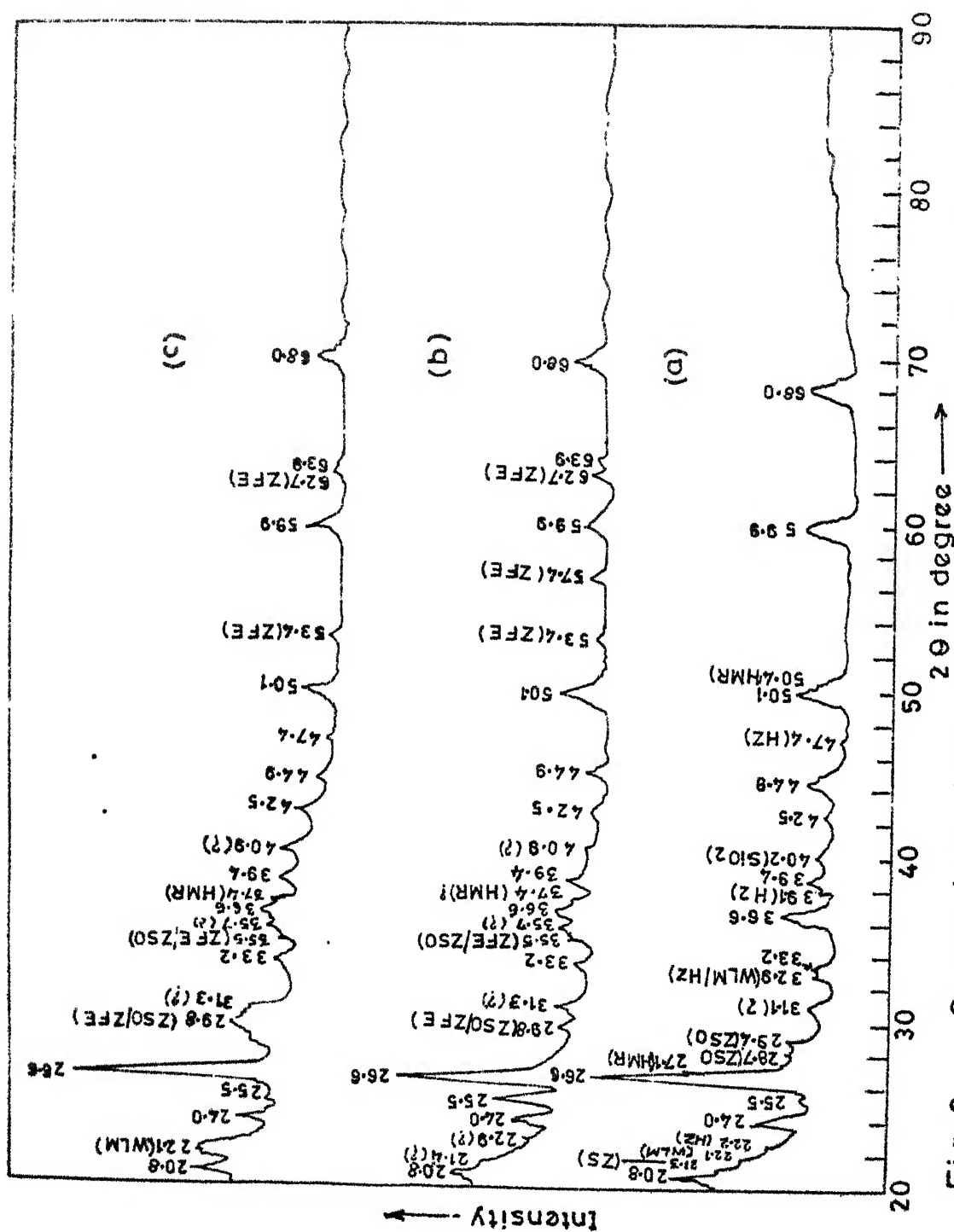


Fig. 8. Comparison between (a) Original Slag Sample (b) Sample Sulfated with H_2SO_4 at 900°C , 2hrs. (c) Residue after leaching of Sulfated Slag.

CHAPTER IV

ACID LEACHING AND FAST LEACHING

4.1 Preamble

Colloidal silica/silicic acid phenomenon, which is probably responsible (19,20,21,24,27,30) for low recovery of zinc in ordinary sulfuric acid leaching of siliceous material, can be handled chemically either by (i) adjusting parameters like pH, temperature, time and addition of polyvalent ions, or (ii) controlling the nature of zinc silicate-sulfuric acid leaching in a water-starved system.

In the first case, there are two distinct approaches, which have been tried. Some people (19,33) have avoided the polymerization of soluble silica, by controlling its amount in the solution (i.e. low solid/liquid ratio), using low temperature (40-50°C), optimising leaching time, and maintaining the end point pH in leaching close to 2.0. Soluble silica which is quite stable at pH 2 or less in a solution containing 100-200 ppm is precipitated in an easily filterable form by raising the pH from 2.0 to 4.0-5.5; others (20) have allowed the polymerization i.e. carried out leaching at high temperature, used higher solid/liquid ratio and polyvalent ions like Al^{3+} which absorb on negatively charged colloidal silica, more preferentially than other ions. Here also, raising of pH from 2.0 to 4.0-5.5 (just below the pH, where aluminium hydroxide is precipitated in the absence of silicic acid) result in the

precipitation of metal silicate complex.

In the water-deficient system, the leaching silicate minerals yields silica in easily filterable form and not in the form of silicic acid. Taking advantage of this fact, the process of fast leaching has been developed.

We have experimented all these ideas with ancient slag, and tried to establish the effect of temperature, addition of Al^{3+} ions and neutralisation in sulfuric acid leaching and acid/solid, water/solid ratios, aging temperature and time in fast leaching.

4.2 Experimental Details:

A. Acid Leaching:

Slag leaching experiments consisted of the following stages (shown in Fig.9):

- i) Leaching Stage
- ii) Neutralisation or Coagulation Stage
- iii) Solid - liquid separation or filtration stage.

i) Leaching Stage:

Leaching of slag was carried out in 1L reaction kettle at different temperatures (50-90°C) using sulfuric acid (1.5N) or a mixture of sulfuric acid (1.5N) and aluminium sulfate ($\text{Al}_2(\text{SO}_4)_3 \cdot 16 \text{H}_2\text{O}$, 3.0 gm/50 gm. of slag). The latter has been referred as modified sulfuric acid. Duration of leaching was 3.0 hours and during this period, pulp density of 10% was maintained.

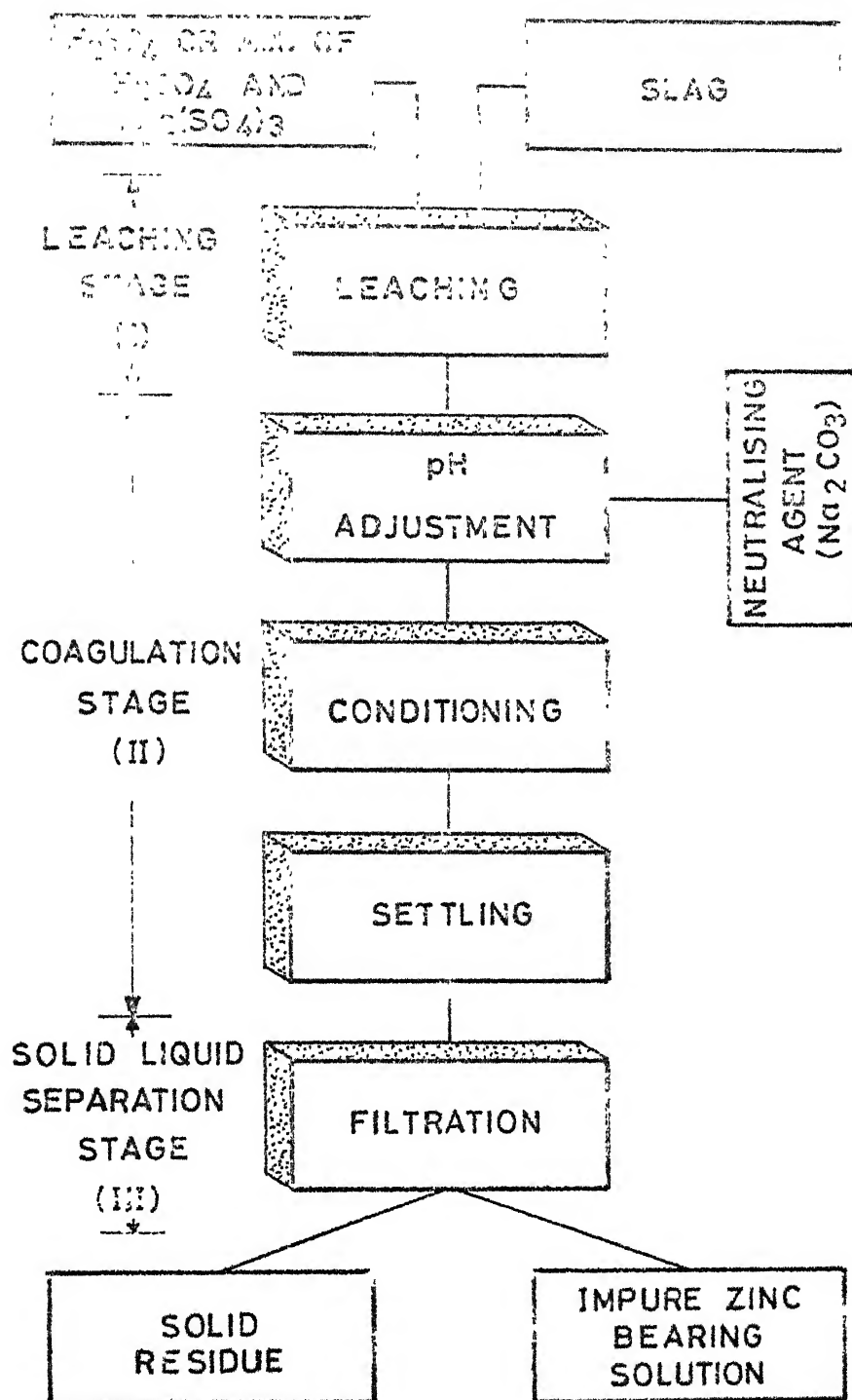


FIG. 9 . SCHEMATIC DIAGRAM OF STEPS INVOLVED IN ACID LEACHING.

Slag sample (50 g) used in leaching experiment was obtained after proper mixing and cone-quartering of approximately 3.5 Kg slag ground to - 200 mesh size. 'Twin' corresponding to a particular sample was retained for chemical analysis.

ii) Neutralisation or Coagulation Stage

One fifth of the pulp obtained after leaching was treated in this stage. This involved three sub-stages i.e.

- pH adjustment
- conditioning
- settling.

Neutralisation (pH, 3.5-5.5), was done using sodium carbonate (6 gm/100 ml of pulp at 35°C). Conditioning of pulp, adjusted to a particular pH, was done at $50^{\circ}\text{C} \pm 10^{\circ}\text{C}$ for one hour. Continuous stirring was done during this period.

Pulp obtained after conditioning was allowed to settle for one hour.

iii) Solid-liquid Separation or Filtration Stage:

Solid obtained after filtration was washed with adequate amounts of water. It has been found out that for washing of 100 ml of pulp, at least same amount of water is required for washing the solid (Fig.10) (Table 5).

Temperature of leaching and pH in neutralisation stage are the only parameters which have been studied both for sulfuric acid leaching and modified sulfuric acid leaching. Experimental conditions have been tabulated in Table 6A, 7A, 8A and 9A.

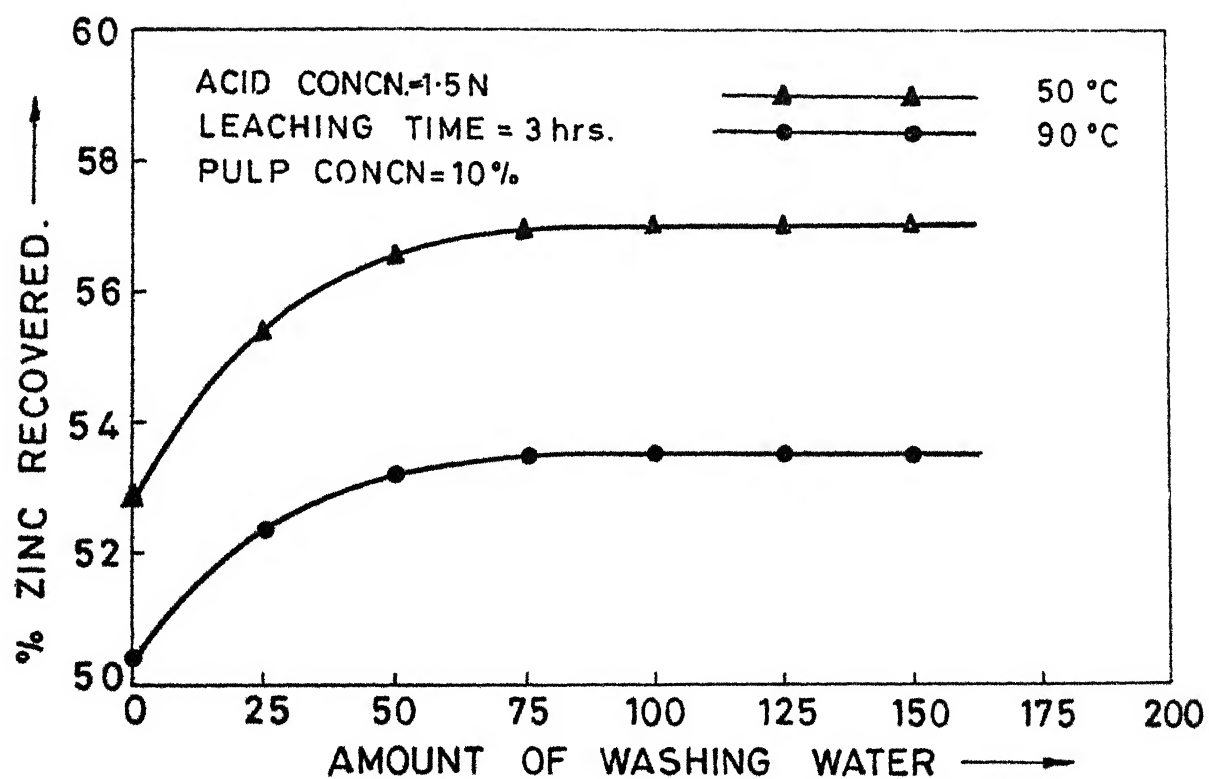


FIG.10.EFFECT OF AMOUNT OF WASHING WATER ON ZINC RECOVERY IN SULFURIC ACID LEACHING. OF SLAG.

B. Fast Leaching:

The following steps were involved (Fig.11):

Premix — Slurry — Aging —
Water Extraction — Filtration.

Premix, slurry leach and aging steps have been jointly referred as 'fast leaching' in further discussion.

10-30 ml of sulfuric acid (sp.gr.1.89) was mixed with different amount (5-35 ml) of water (Premix). Mixing of sulfuric acid with water results in generation of heat and hence temperature rise of acid-water mixture.

Without allowing temperature of acid-water mixture to fall, 50 g slag, obtained after cone-quartering of 2.0-3.0 Kg slag was added to it and mixed with a glass rod rapidly (slurry leach). The size analysis of slag is given below:

Size Range	%
- 150 + 200 mesh	25
- 200	75

The reaction of slag in slurry leach resulted in a further change of temperature. The rise in temperature varied from 90-140°C for the above mentioned quantities of water, acid and slag.

For a typical case, variation of temperature of slurry leach mass with time is shown in Table 14. In the first half an hour temperature falls from 133°C to 62°C.

The slag-acid-water mixture obtained after slurry leach is a thick paste which is aged at a particular temperature

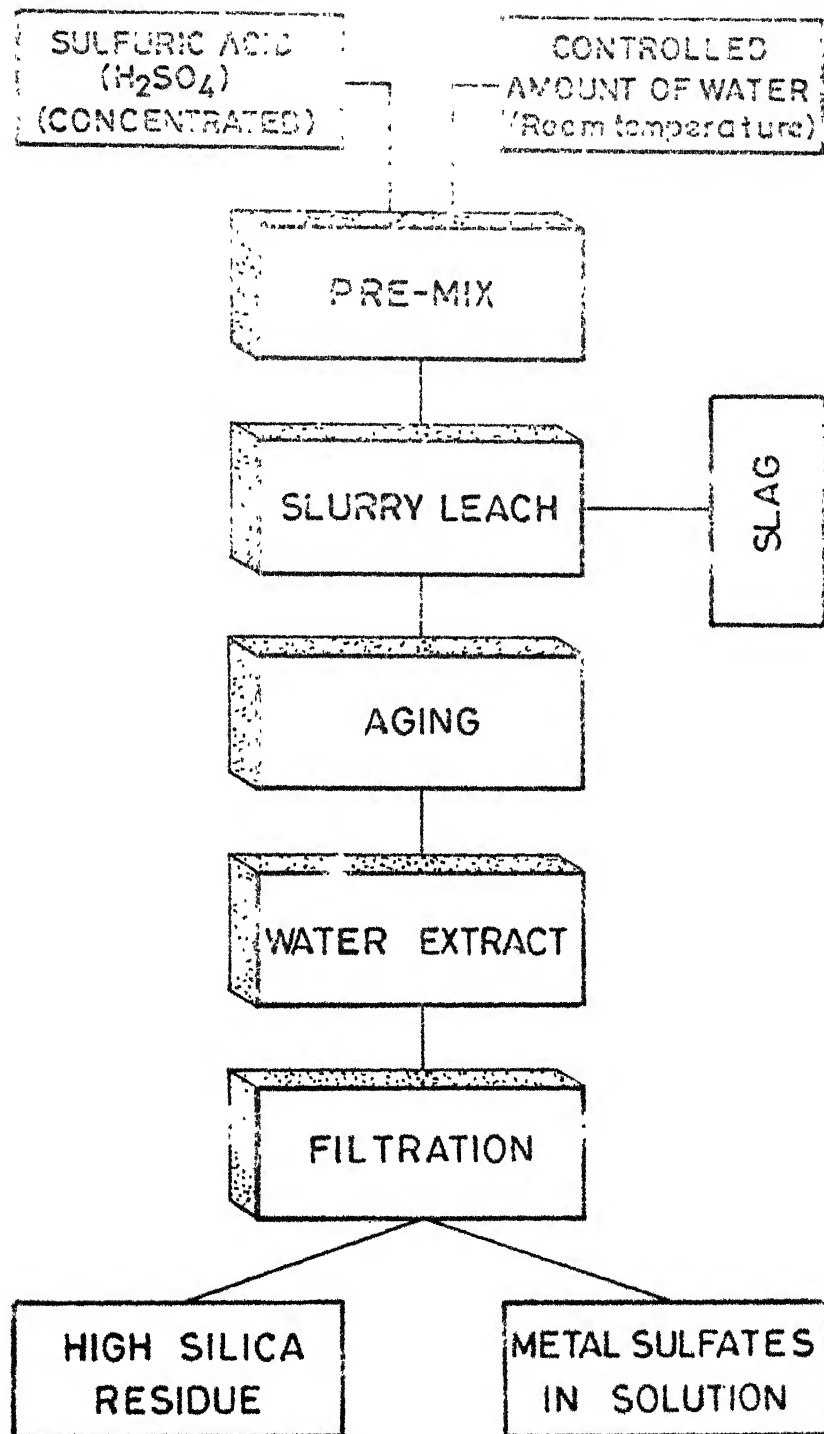


FIG. 11 . SCHEMATIC DIAGRAM OF STEPS INVOLVED IN FAST LEACHING OF SLAG.

(40-90°C) for specific time (15-120 minutes). The crumbled mass obtained after aging was water-leached at 90°C, for 1.5 hr, with 500 ml. of water. During water-leaching, continuous stirring was done. Pulp thus obtained after water leaching was filtered. A crystalline white precipitate (probably silica) was observed in filtered solutions after 12-16 hours except for the cases where large acid and less quantity of water (10 ml. or less) was used. This necessitated refiltration. The following parameters were studied:

- water slag ratio (Expt. conditions listed in Table 10A)
- acid-slag ratio (Expt. conditions listed in Table 11)
- aging time (Expt. conditions listed in Table 12)
- aging temperature (Expt. conditions listed in Table 13).

While conducting experiment for effect of amounts of water, (water-slag ratio) in fast leaching, maximum rise in temperature in premix and slurry leach were noted.

C. Acid Leaching and Fast Leaching of Enriched Zinc Silicate Ores:

The ore samples received from Electrolytic Zinc Company of Australia, were subjected to Acid Leaching (Experimental conditions same as in Table 6A, 7A, S.No. 10 and fast leaching (Experimental conditions same as in Table 10A, S.No. 6). In these experiments, the amount of ore treated was less (20 g) and a pulp density of 4% was maintained. Since the purity of the ore samples was quite high, the purpose of these experiments was to find out the behaviour of willemite and

hemimorphite phases in acid leaching and fast leaching and explain our experimental data for slag system.

D. Elemental Analysis in the Product Solution:

After leaching of Zawar ancient slag by the following methods:

- (a) Modified sulfuric acid leaching at 80°C without neutralisation (Table 6A, S.No.9)
- (b) Modified sulfuric acid leaching at 80°C with neutralisation (Table 7A, S.No.9)
- (c) Modified sulfuric acid leaching at 90°C without neutralisation (Table 6A, S.No.10)
- (d) Modified sulfuric acid leaching at 90°C with neutralisation (Table 7A, S.No.10)
- (e) Fast leaching experiment with acid/slag ratio : 0.78 and water/slag ratio : 0.1 (Table 10A, S.No.6)

Metal analysis in the leached solution was attempted. Results are incomplete. Partial results are given in Table 16.

E. Adsorbability of Zinc Ion in Silicic Acid Colloidal Solution:

Experiments on the above aspect are incomplete. The experiments are designed to find out whether poor recovery of zinc is due to chelation and adsorption of Zn^{++} on silicic acid in the colloidal phase.

4.3 Results:

A. Acid Leaching: The result of acid leaching shown in Figs.12 and 13 (Tables 6B, 7B, 8B, 9B) are summarized below:

1. In sulfuric acid leaching without neutralisation step, zinc recovery decreases with increasing temperature (Fig.12(a)).
2. Neutralisation step, when coupled with sulfuric acid leaching, enhance the zinc recovery, but here also zinc recovery decreases with increasing temperature (Fig.12(b)).
3. Addition of Al^{3+} ions improves zinc recovery, specially at higher temperatures (Fig.12(c)).
4. Neutralisation in modified sulfuric acid leaching still further enhances the zinc recovery, and this increases with increasing temperature (Fig.12(a)).
5. All the above mentioned findings are supported in the results obtained in studying effect of pH.
6. There is an optimum pH ($\simeq 4.5$) of neutralisation, which gives maximum recovery of zinc ($\simeq 71\%$) at $50^{\circ}C$ and $90^{\circ}C$ in sulfuric acid leaching (Fig.13(a) and 13(b)).

Modified sulfuric acid leaching at $90^{\circ}C$, shows a similar trend i.e. recovery is maximum ($\simeq 83\%$) at pH ($\simeq 4.5$) (Fig.13(d)). However, neutralisation pH, seems to have no effect at $50^{\circ}C$ (Fig.13(c)).

B. Fast Leaching: Results of fast leaching experiments performed in different conditions are shown in Fig.14 to Fig.17, Tables 10B, 11, 12 and 13.

The slag analysis in Table 10B, appeared to be on the low side at first, and to verify this, both leach solution and solid residues were analysed for zinc and used in recovery calculations. Reasonable match between the recoveries calculated from two methods, proved the slag analysis to be correct. The effect of various parameters is summarised below:

1. Zinc recovery decreases with increasing water/slag ratio in fast leach, for two different concentration of sulfuric acid (Fig.14).
2. Decrease in acid/slag ratio in fast leach decreases zinc recovery (Fig.14 and 15).
3. Zinc recovery increases with increasing aging temperature and time (Figs.16 and 17).
4. Among the various parameters studies, the effect of water/slag ratio is most significant.

Apart from the tabulated and plotted results, the following observations were made:

1. Filterability of a leached solution deteriorates
 - (a) with decreasing acid concentration, and
 - (b) increasing amount of water, in fast leach for the same amount of slag.

2. The rise of temperature in slurry leach treatment is not uniform throughout the mass. Even though the slag-water-acid, mass was continuously mixed, the measured and stated temperature rise should be considered as approximate.
3. The amount of white crystalline material (possibly silica) which necessitated refiltration increases with (a) decreasing acid concentration, and (b) increasing amount of water in fast leach for the same amount of slag.

C. Leaching and X-ray result for Enriched Zinc Silicate Ores:

Fig.18 H(a,b,c and d) and Fig.18 W(a,b,c and d) shows almost complete disappearance of zinc bearing phases including the silicate phases, namely Hemimorphite and willemite after leaching. The residue obtained after dissolution of ore sample containing hemimorphite mostly contained amorphous phases (Fig.18); the ore sample containing willemite, examined after leaching showed peaks of lead sulfate and few unidentified phases.

Recovery values shown in Table 15, further confirms the fact that these phases are easily soluble. Keeping in mind the large amount of dilution required for analysing these samples by atomic absorption spectrophotometry recoveries are expected to lie in error limit $\pm 10\%$. In case of sample containing hemimorphite, neutralisation seems to have some positive effect on zinc recovery.

TABLE 5

Experimental Conditions and Results - Effect of Amount of Washing Water in Sulfuric Acid Leaching
At Different Temperatures

Acid Conc. - 1.5N, Time of Leaching - 3.0 hrs, Size of Slag - 200 mesh, Pulp con.: 10%, Vessel Capacity 1L, Settling Time Prior to Filtration - 1 hr.

Amount of washing water/100 ml of pulp	I				II			
	Temperature - 50°C				Temperature - 90°C			
	% Zn in slag	% of total zinc recovered	Total Recovery (%)	% Zn in slag	% of total zinc recovered	Total Recovery (%)	Total Recovery (%)	Total Recovery (%)
0	2.79	53.04	53.04	2.79	50.44	50.44	50.44	50.44
25	2.79	2.41	55.45	2.79	2.028	52.46	52.46	52.46
50	2.79	1.375	56.78	2.79	0.80	53.26	53.26	53.26
75	2.79	0.178	56.95	2.79	0.134	53.39	53.39	53.39
100	2.79	0.028	56.98	2.79	0.028	53.42	53.42	53.42
125	2.79	0.029	57.01	2.79	0.027	53.44	53.44	53.44
150	2.79	0.009	57.02	2.79	0.010	53.45	53.45	53.45

TABLE 6A

Experimental Conditions in Sulfuric Acid Leaching and Modified* Sulfuric Acid Leaching at Different Temperature (No. Neutralisation)

Sl. No.	Leaching Stage						Settling time (hrs)		
	Acid	Conc. x(N)	Time (hrs.)	Size of slag (mesh)	Pulp Conc. P (%)	Vessel Capacity			
						Temp. (°C)	Aluminium sulfate added gm/1		
1	H ₂ SO ₄	1.5	3.0	-200	10	1L	50	0	1.0
2	H ₂ SO ₄	1.5	3.0	-200	10	1L	60	0	1.0
3	H ₂ SO ₄	1.5	3.0	-200	10	1L	70	0	1.0
4	H ₂ SO ₄	1.5	3.0	-200	10	1L	80	0	1.0
5	H ₂ SO ₄	1.5	3.0	-200	10	1L	90	0	1.0
6	H ₂ SO ₄	1.5	3.0	-200	10	1L	50	6.0	1.0
7	H ₂ SO ₄	1.5	3.0	-200	10	1L	60	6.0	1.0
8	H ₂ SO ₄	1.5	3.0	-200	10	1L	70	6.0	1.0
9	H ₂ SO ₄	1.5	3.0	-200	10	1L	80	6.0	1.0
10	H ₂ SO ₄	1.5	3.0	-200	10	1L	90	6.0	1.0

TABLE 6B

Results - Effect of Temperature in Sulfuric Acid Leaching and Modified Sulfuric Acid Leaching (No. Neutralisation)

Temperature (°C)	I			II		
	Sulfuric Acid Leaching			Modified Sulfuric Acid Leaching		
	% Zn in slag	Zinc dissolved gm/100 gm of slag	Recovery (%)	% Zn in slag	Zinc Dissolved gm/100 gm of slag	Recovery (%)
50	2.60	1.42	54.60	2.60	1.405	54.0
60	2.60	1.435	55.19	2.60	1.46	56.1
70	2.60	1.35	51.90	2.79	1.60	57.4
80	2.79	-	-	2.79	2.09	74.9
90	2.79	1.40	50.17*	2.98	2.21	74.2

* Experiment was performed at 86°C.

TABLE 7A

Experimental Conditions in Sulfuric Acid Leaching and Modified Sulfuric* Acid Leaching
(at different temperatures) coupled with Neutralisation or Coagulation Step

II													
I													
Coagulation Stage													
Leaching Stage													
S.No.	Acid	Conc. x(N)	Time (hrs)	Size of slag (mesh)	Pulp conc. P(%)	Vessel capa- city	Temp. (°C)	Aluminium sulfate added g/l	Neutra- lizing agent	pH	Temp. (°C)	Condi- tioning time	Settl- ing time
1	H ₂ SO ₄	1.5	3.0	-200	10	1L	50	0	Na ₂ CO ₃	5.0	50	1.0	1.0
2	H ₂ SO ₄	1.5	3.0	-200	10	1L	60	0	Na ₂ CO ₃	5.0	50	1.0	1.0
3	H ₂ SO ₄	1.5	3.0	-200	10	1L	70	0	Na ₂ CO ₃	5.0	50	1.0	1.0
4	H ₂ SO ₄	1.5	3.0	-200	10	1L	80	0	Na ₂ CO ₃	5.0	50	1.0	1.0
5	H ₂ SO ₄	1.5	3.0	-200	10	1L	90	0	Na ₂ CO ₃	5.0	50	1.0	1.0
6	H ₂ SO ₄	1.5	3.0	-200	10	1L	50	6.0	Na ₂ CO ₃	5.0	50	1.0	1.0
7	H ₂ SO ₄	1.5	3.0	-200	10	1L	60	6.0	Na ₂ CO ₃	5.0	50	1.0	1.0
8	H ₂ SO ₄	1.5	3.0	-200	10	1L	70	6.0	Na ₂ CO ₃	5.0	50	1.0	1.0
9	H ₂ SO ₄	1.5	3.0	-200	10	1L	80	6.0	Na ₂ CO ₃	5.0	50	1.0	1.0
10	H ₂ SO ₄	1.5	3.0	-200	10	1L	90	6.0	Na ₂ CO ₃	5.0	50	1.0	1.0

* addition of aluminium sulfate in leaching stage.

TABLE 7B

Results - Effect of Temperature in Sulfuric Acid Leaching and Modified Sulfuric Acid Leaching Coupled with Neutralisation Step

Temperature (°C)	I			II		
	Sulfuric Acid Leaching			Modified Sulfuric Acid Leaching		
	% Zn in slag	Zinc dissolved gm/100 of slag	Recovery (%)	% Zn in slag	Zinc dissolved gm/100 of slag	Recovery (%)
50	2.71	2.30	84.8	2.71	2.09	77.12
60	2.97	2.37	79.8	2.97	-	-
70	2.70	2.02	74.8	2.70	2.315	85.7
80	2.70	1.905	70.6	2.70	2.40	88.8
90	2.71	2.06	76.0	2.71	2.565	94.6

TABLE 8A

Experimental Conditions, Effect of Neutralisation pH in Sulfuric Acid Leaching
(coupled with coagulation step) at different temperatures

II													
I										Coagulation Stage			
Leaching Stage										Coagulation Stage			
S. No.	Acid	Conc. x(N)	Time (hr.)	Size of slag (mesh)	Pulp conc.	Vessel capacity	Temp. (°C)	Neutralizing agent	Conditioning time (hr.)	Temp. (°C)	pH*		Settling time
											initial	after conditioning	
1	H ₂ SO ₄	1.5	3.0	-200	10	1L	50	Na ₂ CO ₃	1.0	50	3.5	3.3	1.0
2	H ₂ SO ₄	1.5	3.0	-200	10	1L	50	Na ₂ CO ₃	1.0	50	4.0	3.8	1.0
3	H ₂ SO ₄	1.5	3.0	-200	10	1L	50	Na ₂ CO ₃	1.0	50	4.6	4.3	1.0
4	H ₂ SO ₄	1.5	3.0	-200	10	1L	50	Na ₂ CO ₃	1.0	50	5.15	5.0	1.0
5	H ₂ SO ₄	1.5	3.0	-200	10	1L	50	Na ₂ CO ₃	1.0	50	5.6	5.3	1.0
6	H ₂ SO ₄	1.5	3.0	-200	10	1L	90	Na ₂ CO ₃	1.0	50	3.6	3.4	1.0
7	H ₂ SO ₄	1.5	3.0	-200	10	1L	90	Na ₂ CO ₃	1.0	50	4.15	3.85	1.0
8	H ₂ SO ₄	1.5	3.0	-200	10	1L	90	Na ₂ CO ₃	1.0	50	4.6	4.45	1.0
9	H ₂ SO ₄	1.5	3.0	-200	10	1L	90	Na ₂ CO ₃	1.0	50	5.1	4.9	1.0
10	H ₂ SO ₄	1.5	3.0	-200	10	1L	90	Na ₂ CO ₃	1.0	50	5.7	5.3	1.0

* measured at 35°C.

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TABLE 8B

Results, Effect of Neutralisation pH in Sulfuric Acid Leaching (Coupled with Coagulation Step) at Different Temperatures

I										
Temperature 50°C					Temperature 90°C					
pH		% zinc in slag	Zinc dissolved/ 100 g of slag	Recovery (%)	pH		% Zinc in slag	Zinc dissolved/ 100 g of slag	Recovery (%)	
initial	final				initial	final				
3.5	3.3	2.48	1.70	68.5	3.6	3.4	2.475	1.83	74.1	
4.0	3.8	2.48	1.72	69.4	4.15	3.85	2.475	1.73	70.1	
4.6	4.3	2.48	1.76	71.2	4.6	4.45	2.56	1.82	71.4	
5.15	5.0	2.46	1.73	70.9	5.1	4.9	2.56	1.77	69.3	
5.6	5.3	2.46	1.69	68.7	5.7	5.3	2.62	1.77	67.9	

TABLE 9A

A Experimental Conditions, Effect of Neutralisation pH in Modified Sulfuric Acid Leaching
(Sulfuric Acid and Aluminium Sulfate Leaching) Different Temperatures

II														
LEACHING STAGE							COAGULATION STAGE							
S. No.	Acid	Conc. x(N)	Time (hr.)	Size of slag (mesh)	Pulp conc. P(%)	Vessel capacity	Temp. (°C)	Amount of aluminium sulfate added (g)*	Neutra- lizing agent	Condi- tioning time(hr)	Temp. (°C)	pH	** after initi- tion- ing	Settl- ing time (hrs.)
1	H ₂ SO ₄	1.5	3.0	-200	10	1L	50	6.0	Na ₂ CO ₃	1.0	50	3.6	3.4	1.0
2	H ₂ SO ₄	1.5	3.0	-200	10	1L	50	6.0	Na ₂ CO ₃	1.0	50	4.15	4.0	1.0
3	H ₂ SO ₄	1.5	3.0	-200	10	1L	50	6.0	Na ₂ CO ₃	1.0	50	4.6	4.5	1.0
4	H ₂ SO ₄	1.5	3.0	-200	10	1L	50	6.0	Na ₂ CO ₃	1.0	50	5.15	4.95	1.0
5	H ₂ SO ₄	1.5	3.0	-200	10	1L	50	6.0	Na ₂ CO ₃	1.0	50	5.65	5.45	1.0
6	H ₂ SO ₄	1.5	3.0	-200	10	1L	50	6.0	Na ₂ CO ₃	1.0	50	3.6	3.45	1.0
7	H ₂ SO ₄	1.5	3.0	-200	10	1L	50	6.0	Na ₂ CO ₃	1.0	50	4.2	4.2	1.0
8	H ₂ SO ₄	1.5	3.0	-200	10	1L	50	6.0	Na ₂ CO ₃	1.0	50	4.6	4.45	1.0
9	H ₂ SO ₄	1.5	3.0	-200	10	1L	50	6.0	Na ₂ CO ₃	1.0	50	5.1	4.85	1.0
10	H ₂ SO ₄	1.5	3.0	-200	10	1L	50	6.0	Na ₂ CO ₃	1.0	50	5.8	5.7	1.0

* per 100 g of slag.

** measured at 35°C.

TABLE 9B

Results, Effect of Neutralisation pH in Modified Sulfuric Acid Leaching (H_2SO_4 + Aluminium Sulfate, Leaching) at Different Temperatures

II									
I					Temperature 90°C				
Temperature 50°C					Temperature 90°C				
pH		% Zinc in slag		Zinc dissolved/100 g of slag	Recovery (%)	pH		% Zinc in slag	Zinc dissolved/100 g of slag
Initial	Final					initial	final		
3.6	3.4	2.48		1.82	73.8	3.6	3.45	2.475	1.915
4.15	4.0	2.48		1.78	71.8	4.2	4.2	2.475	2.029
4.6	4.5	2.48		1.85	74.6	4.6	4.45	2.56	2.073
5.15	4.95	2.46		1.837	74.7	5.1	4.85	2.56	2.015
5.65	5.45	2.46		1.845	75.0	5.8	5.7	2.62	1.44
									55.0

TABLE 10 A

Experimental Conditions, Effect of Amount of Water used in Fast Leach

1A			1B			2			3		
Pre-Mix Stage			Slurry Leach			Aging Stage			Water Extract		
H ₂ SO ₄ used (ml.)	Water added (ml.)	Observed temp. rise (°C)	Size of slag ()	Amount slag (g)	Observed temp. rise (°C)	Temp. (°C)	Time (min.)	Amount of water used	Temp. (°C)	Time (hr.)	
1 15.0	10	104	-150	50.0	104	45	12-15	500	90	1.5	
2 15.0	15	105	-150	50.0	108	45	12-15	500	90	1.5	
3 15.0	20	107	-150	50.0	104	45	12-15	500	90	1.5	
4 15.0	25	104	-150	50.0	95	45	12-15	500	90	1.5	
5 15.0	35	98	-150	50.0	90	45	12-15	500	90	1.5	
6 20.0	5	111	-150	50.0	129	45	12-15	500	90	1.5	
7 20.0	10	104	-150	50.0	112	45	12-15	500	90	1.5	
8 20.0	15	108	-150	50.0	-	45	12-15	500	90	1.5	
9 20.0	20	114	-150	50.0	115	45	12-15	500	90	1.5	
10 20.0	25	115	-150	50.0	104	45	12-15	500	90	1.5	
11 20.0	35	102	-150	50.0	98	45	12-15	500	90	1.5	

TABLE 10B

Results, Effect of Amount of Water Used in Past Leach

Sl. No.	H ₂ SO ₄ used (ml.)	Water used (ml.)	% Zinc in slag	Zinc* recovery/100g of slag	% Zinc recovered	Zinc** unrecovered/100g of slag	% Zinc unrecovered	Remark
1	15.0	10	2.14	1.655	77.3	0.473	22.0	Recovery values
2	15.0	15	2.14	1.610	75.2	-	-	calculated
3	15.0	20	2.14	1.630	76.1	0.482	22.5	from
4	15.0	25	2.14	1.589	74.1	-	-	analysis of
5	15.0	35	2.14	1.595	74.5	0.586	27.38	solid leach
6	20.0	5.0	2.09	1.695	81.1	-	-	residue and
7	20.0	10.0	2.14	1.705	79.7	0.451	21.0	leach
8	20.0	15.0	2.14	1.675	78.3	-	-	solution
9	20.0	20.0	2.14	1.645	76.9	0.469	21.9	matches
10	20.0	25.0	2.14	1.655	77.3	-	-	reasonable
11	20.0	35.0	2.14	1.625	75.9	0.564	26.3	well

* from analysis of leach solution.

** from analysis of solid residue (\approx 45g/50g of slag) obtained after leaching.

TABLE 11

Experimental Conditions, Effect of Amount of Acid used in fast Leach and Results

Sl. No.	I							II			
	Experimental Conditions							Results			
	Pre-mix Stage	Slurry Leach	Aging Stage	Water Extract			Time	% Zn in	Zinc	Reco-	
	H ₂ SO ₄ used (ml.)	Size of slag	Amount of slag (g)	Temp. (°C)	Time (min.)	Water used (ml.)	Temp. (°C)	(hr.)	slag	recovered g/100g of slag	very (%)
1	10.0	-150	50.0	45	12-15	500	90	1.5	2.12	1.62	76.4
2	15.0	-150	50.0	45	12-15	500	90	1.5	2.14	1.64	76.6
3	20.0	-150	50.0	45	12-15	500	90	1.5	2.14	1.65	77.1
4	25.0	-150	50.0	45	12-15	500	90	1.5	2.12	1.63	76.9
5	30.0	-150	50.0	45	12-15	500	90	1.5	2.12	1.66	78.3

TABLE 13

Experimental Conditions and Results, Effect of Aging Temperature in Fast Leach

Sl. No.	I						II					
	Experimental Conditions						Results					
	Pre-mix Stage		Slurry Leach		Aging Stage		Water Extract		Results			
	H ₂ SO ₄ used (ml.)	Water added	Size of slag()	Amount of slag(g)	Temp. (°C)	Time (min)	Water used (ml.)	Temp. (°C)	Time (hr.)	% Zn in slag	Zinc Recovered g/1000g of slag	Recovery (%)
1	20.0	10.0	-150	50.0	50	30	500	90	1.5	2.09	1.63	78.0
2	20.0	10.0	-150	50.0	60	30	500	90	1.5	2.09	1.66	79.2
3	20.0	10.0	-150	50.0	70	30	500	90	1.5	2.09	1.68	80.1
4	20.0	10.0	-150	50.0	80	30	500	90	1.5	2.09	1.67	79.8
5	20.0	10.0	-150	50.0	90	30	500	90	1.5	2.09	1.69	80.6

TABLE 14Variation of Temperature of Slurry Leach Mass in Fast Leaching

Water/slag ratio. 0.1, Acid/slag ratio: 0.78, Weight of slag:50g,
Surrounding temperature - Room temperature ($\approx 33^{\circ}\text{C}$)

Time (Minutes)	Temperature
0	133
2	127
4	119
6	110
8	103
10	96
15	83
20	74
25	67
30	62
40	55
50	49
60	47

TABLE 16

Metal Analysis in the Product Solution

Quantity of slag used: 50g,

Total Volume: 500 c.c.

Method described before as	Broad Description	Experimental conditions	% Zn in slag	% Fe in slag	Zn Conc. g/l.	Zinc recovery (%)	Fe conc. g/l	Fe recovery (%)
(a)	Modified sulfuric acid leaching, 80°C, without neutralisation	(same as Table 6A, S.No.9)	2.375	4.8	1.81	76.42	4.64	96.66
(b)	Modified sulfuric acid leaching, 80°C, with neutralisation	(same as Table 7A, S.No.9)	2.375	4.8	1.91	80.63	2.89	60.20
(c)	Modified sulfuric acid leaching, 90°C, without neutralisation	(same as Table 6A, S.No.10)	2.375	4.8	1.85	77.89	4.59	95.52
(d)	Modified sulfuric acid leaching, 90°C, with neutralisation	(same as Table 7A, S.No.10)	2.375	4.8	2.05	86.3	3.1	64.58
(e)	Fast leaching	(same as Table 10A, S.No.6)	2.24	4.48	1.84	82.14	4.43	98.88

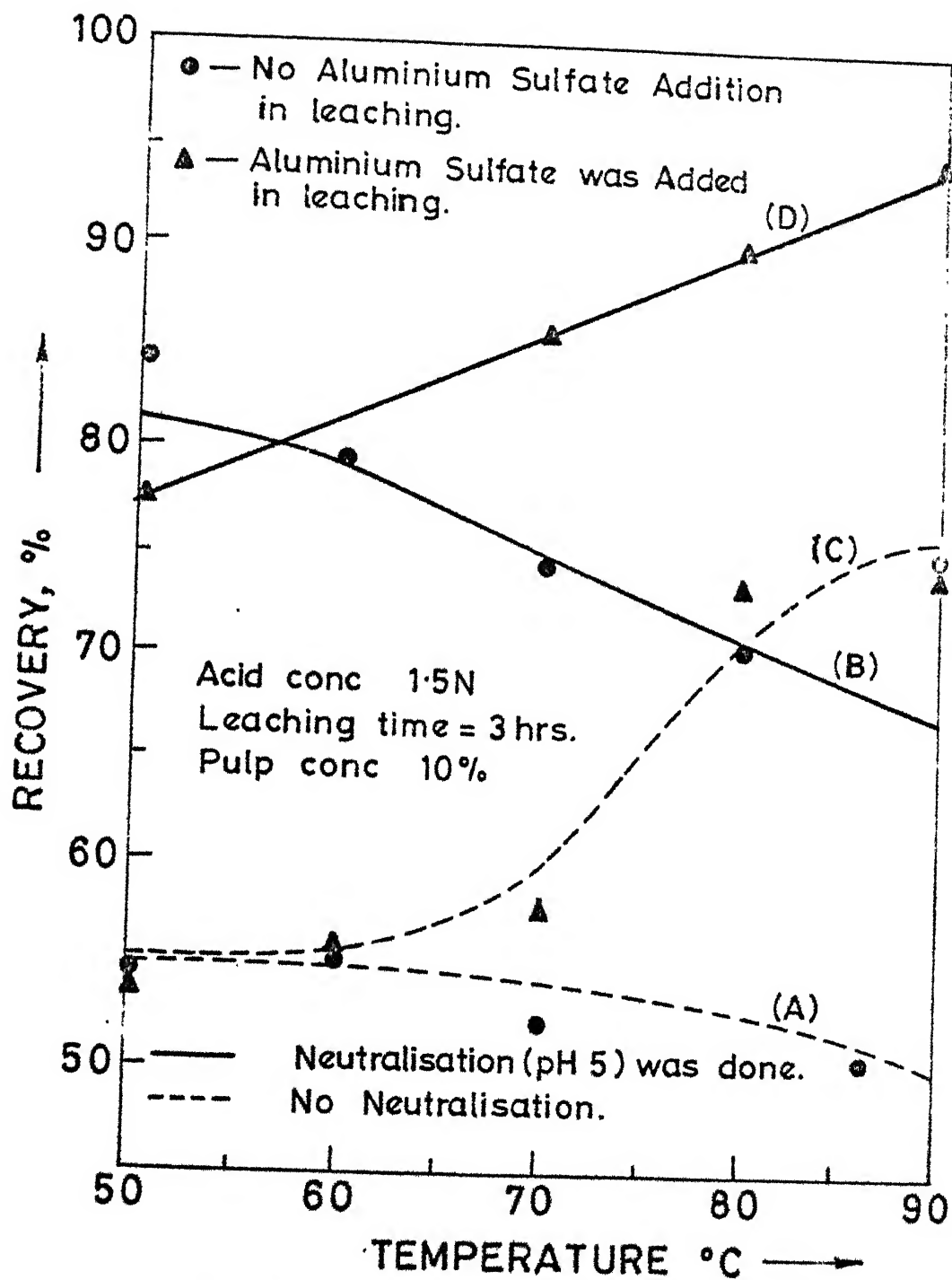


FIG.12. EFFECT OF TEMPERATURE IN SULFURIC ACID LEACHING AND ITS MODIFICATION.

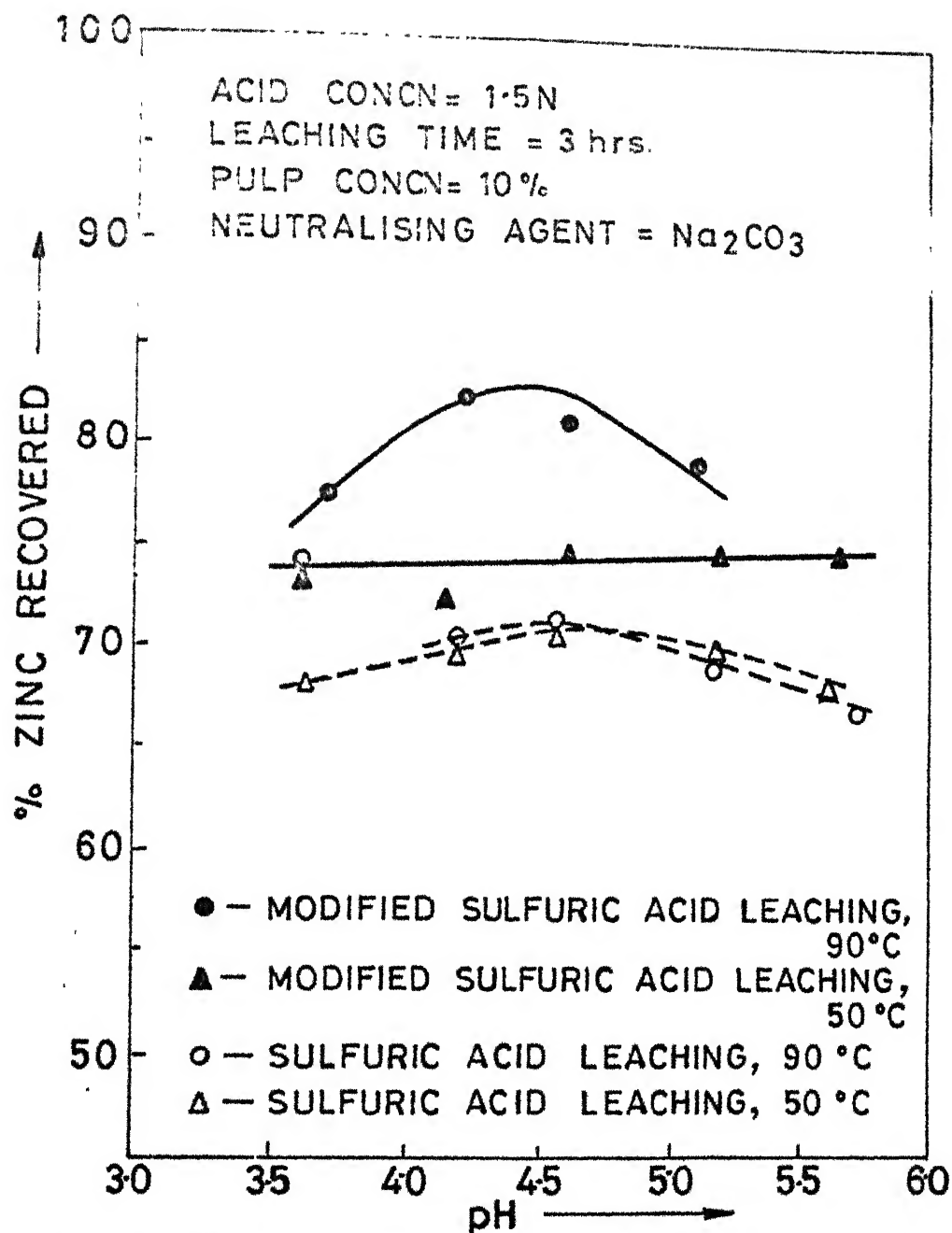
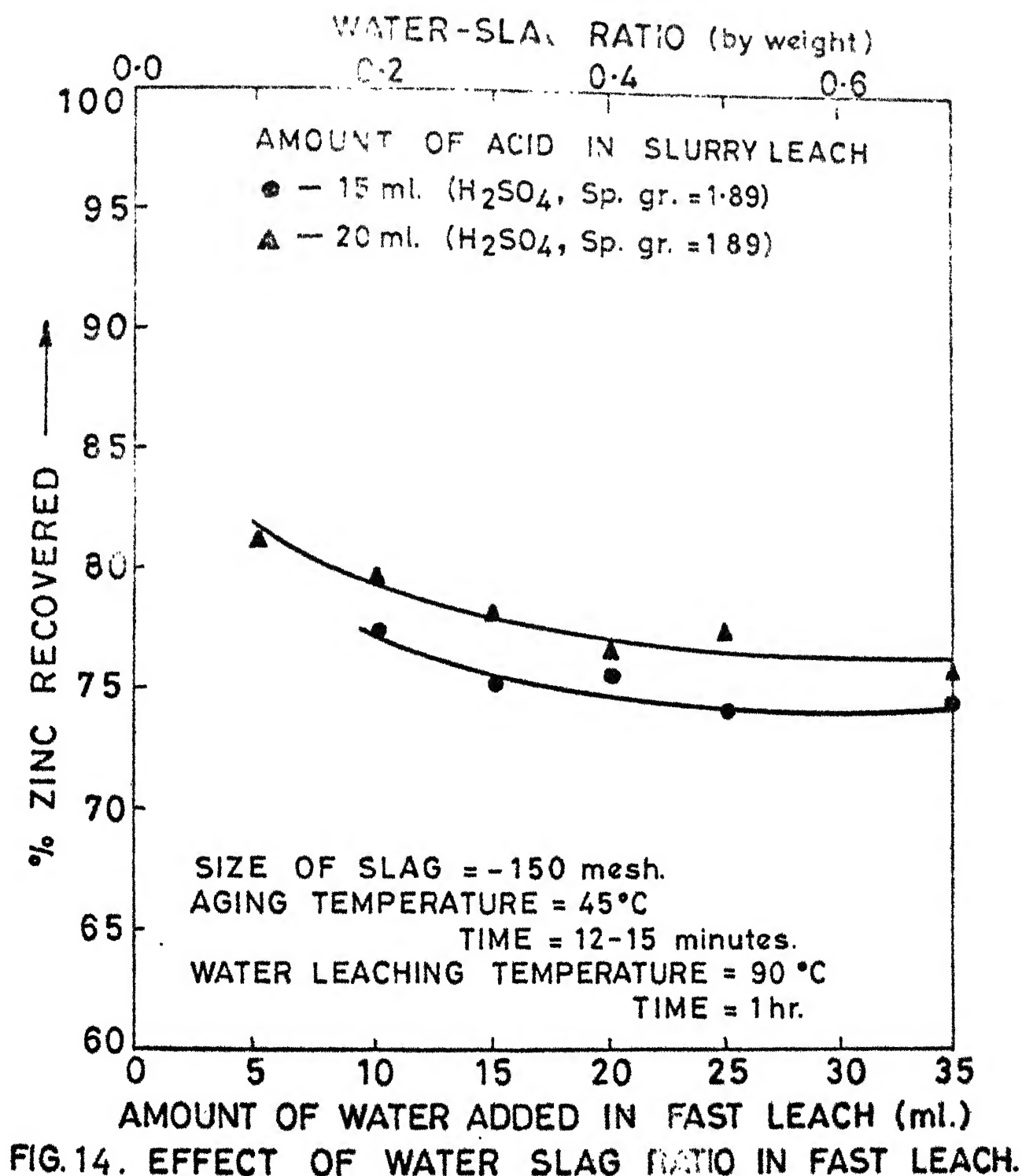


FIG.13. EFFECT OF pH IN SULFURIC ACID LEACHING AND MODIFIED SULFURIC ACID LEACHING COUPLED WITH NEUTRALISATION STAGE.



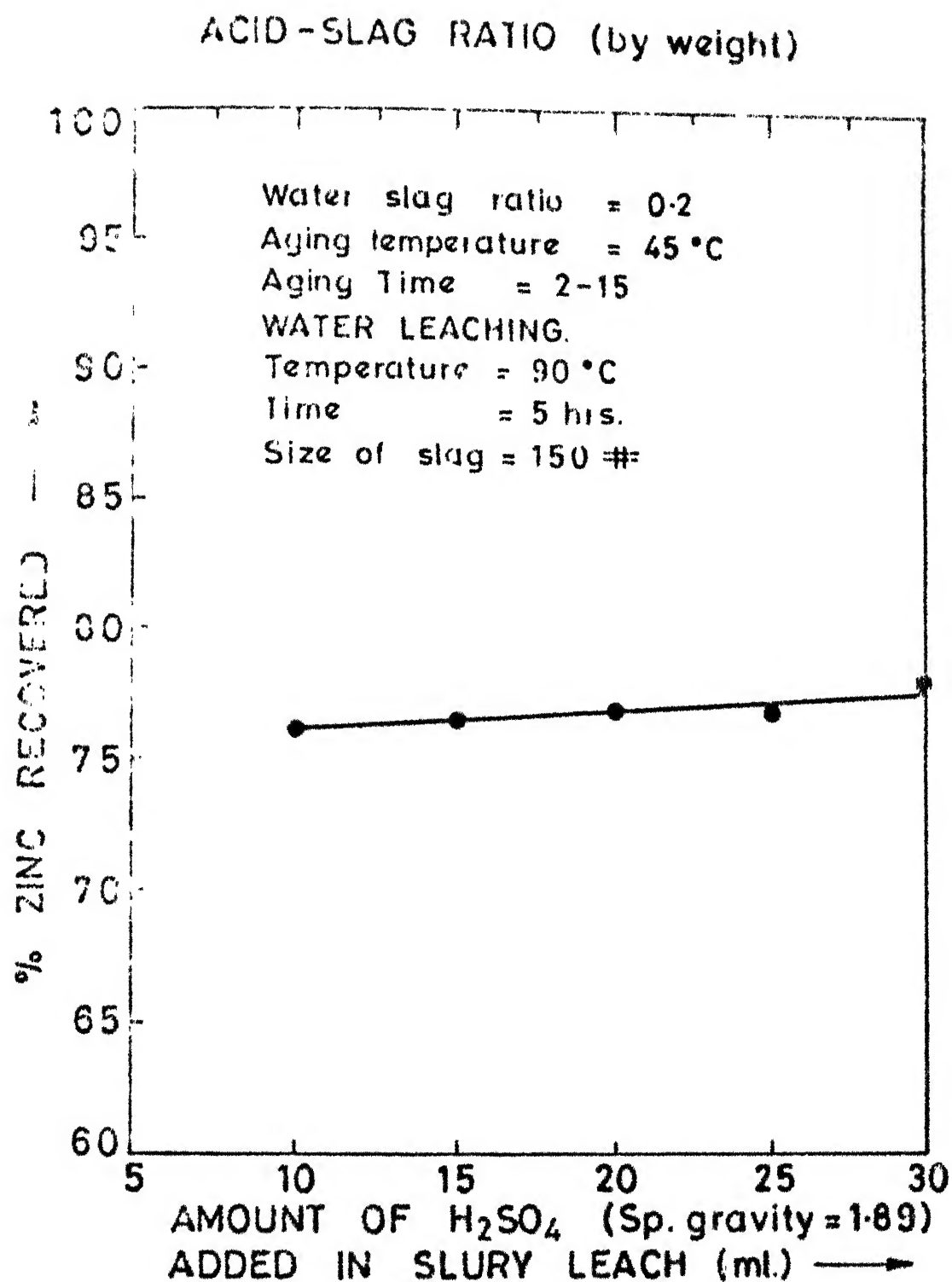


FIG.15. EFFECT OF ACID SLAG RATIO IN FAST LEACHING.

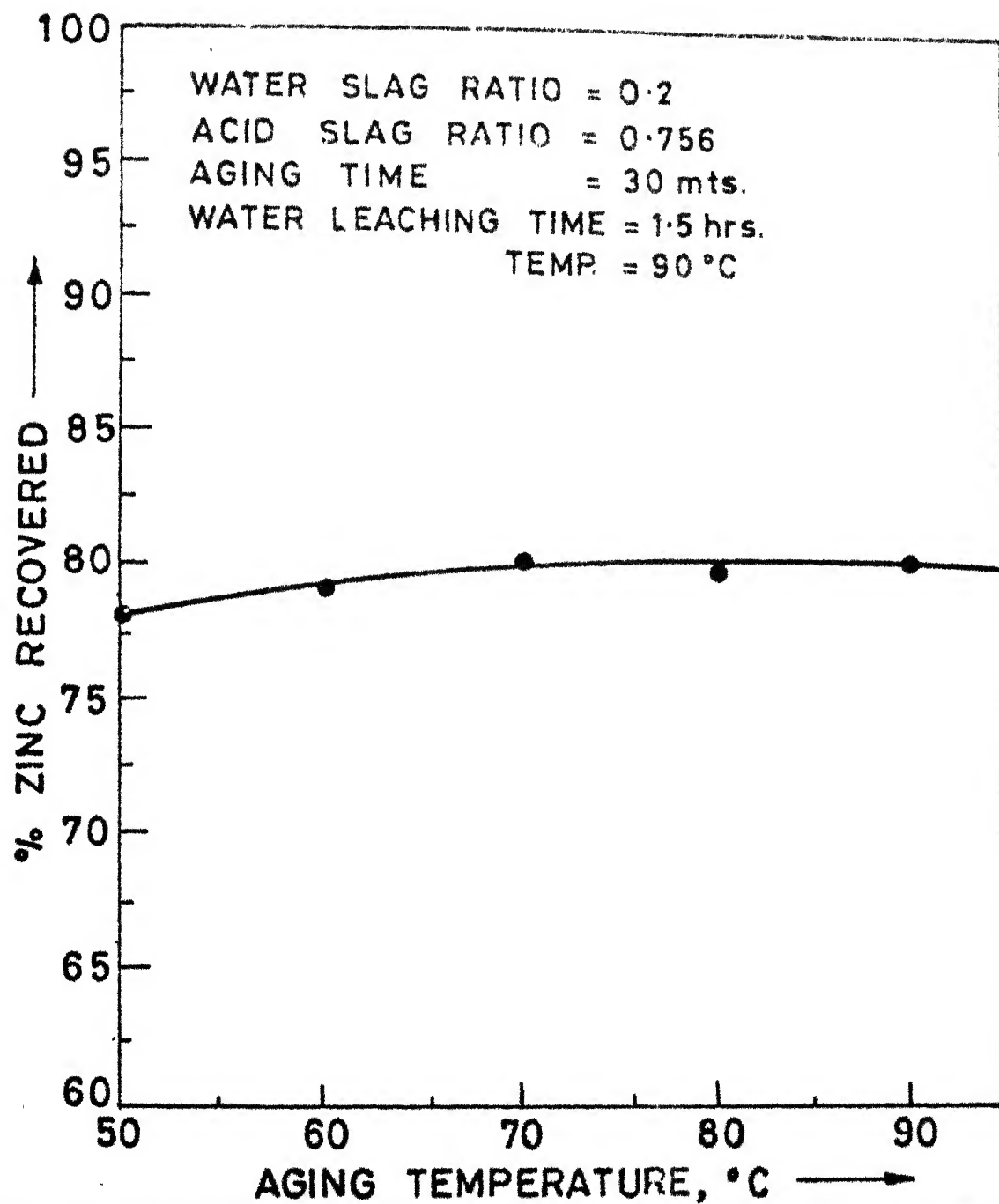


FIG.16. EFFECT OF AGING TEMPERATURE ON ZINC RECOVERY IN FAST LEACHING.

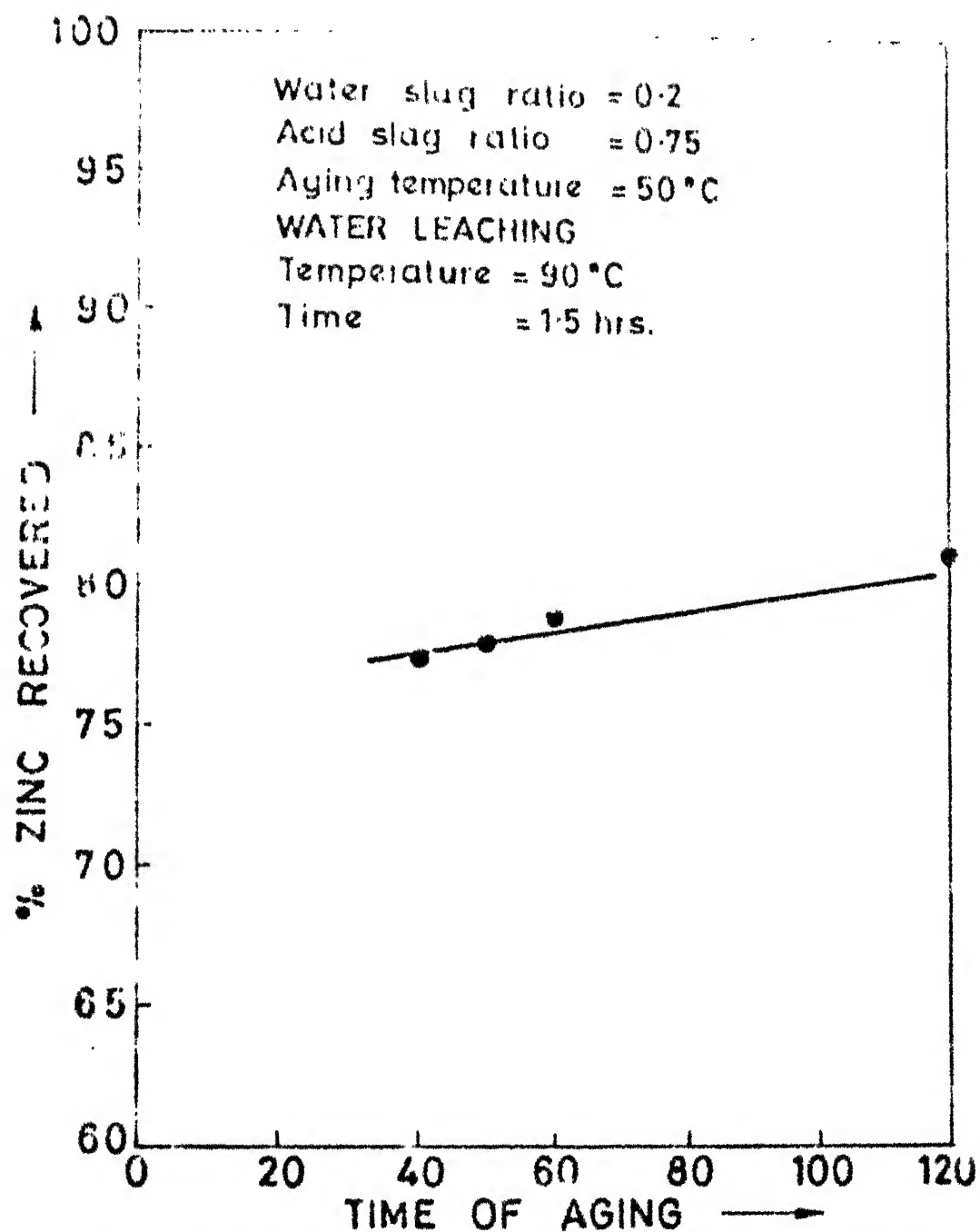


FIG. 17. EFFECT OF AGING TIME IN FAST LEACHING.

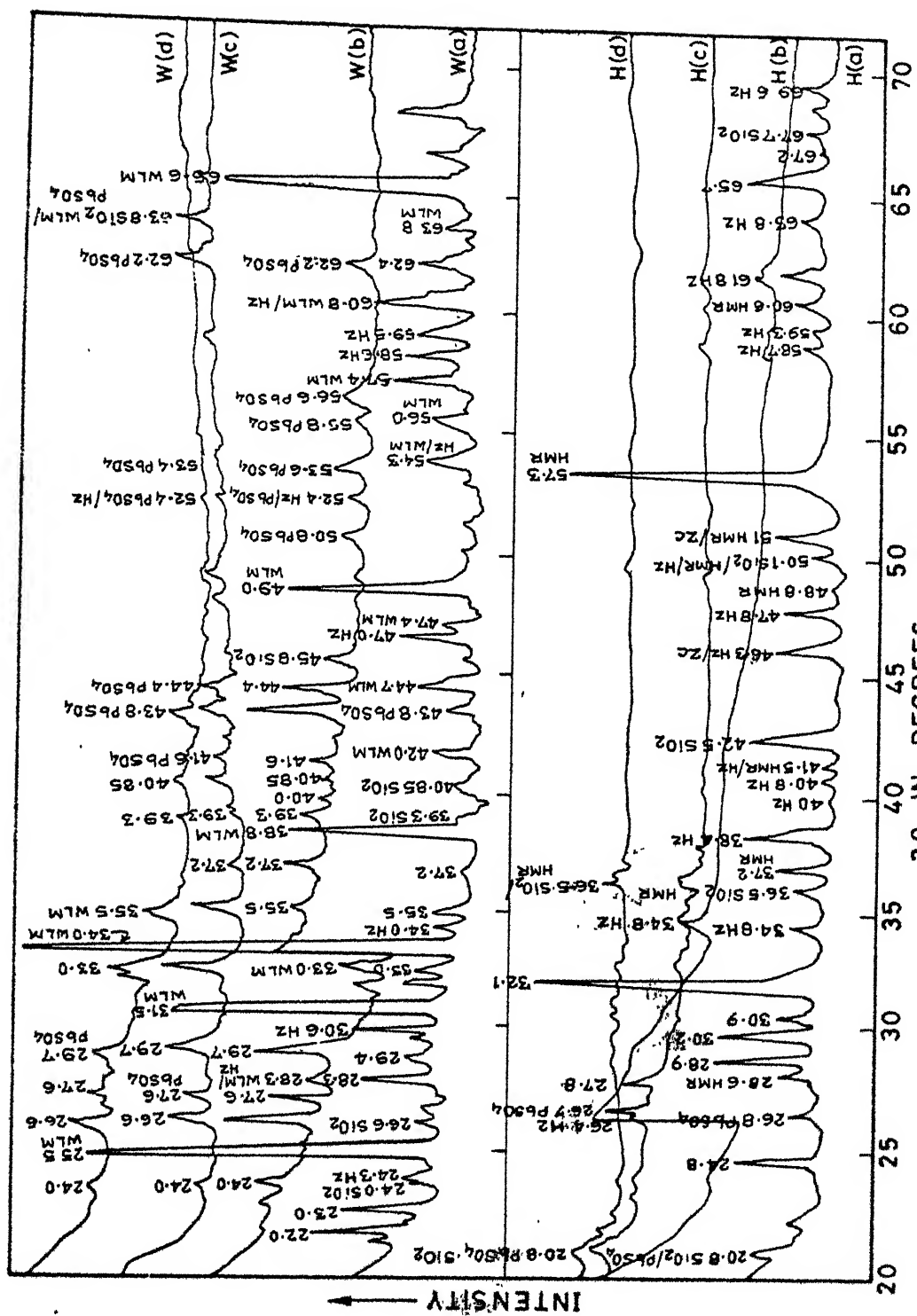


FIG.18 BEHAVIOUR OF Z-SILICATE ORES IN DIFFERENT LEACHING CONDITIONS.
 H(a) ORIGINAL ORE CONTAINING HEMIMORPHITE (O.S.). H(b) O.S. AFTER FAST LEACHING
 H(c) O.S. AFTER ACID LEACHING NO NEUTRALISATION H(d) O.S. AFTER ACID LEACHING & NEUTRALISATION
 W(a) ORE CONTAINING WILLEMITE (O.S.). W(b). O.S. AFTER FAST LEACHING
 W(c) O.S. AFTER ACID LEACHING NO NEUTRALISATION W(d) O.S. AFTER ACID LEACHING & NEUTRALISATION

CHAPTER V

CONCLUSION AND SUGGESTIONS

This thesis outlines the results of investigations pertaining to zinc recovery from ancient slag. Results obtained in this investigation are likely to be applicable for crucible content (residue left in retort metallurgy of zinc) due to similarity of phases (2).

Chemical analysis of the slag has been given in Chapter 1. When metallic elements are considered as their respective oxides, the total material accounts for 75-80% of the slag.

Gangopadhyaya (2) has found out by various techniques like X-ray ^{and} transmission electron microscopy that the following phases are present in the slag.

Hydrated zinc sulfate, $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$; Sphalerite, ZnS , Hemimorphite $\text{Zn}_4(\text{OH})_2 \text{Si}_2\text{O}_7 \cdot \text{H}_2\text{O}$; Hydrozincite, $\text{Zn}_5(\text{CO}_3)_2(\text{OH})_6$ and quartz, SiO_2 .

He (2) has also established that ancient slag is glassy in nature with some crystals inside and zinc is segregated in the slag samples.

Our investigation (Chapter 3, Table 4) reveals that sulfuric acid easily dissolved sulfates and basic carbonate phases of zinc.

Mathew and Elsner's view (Ref.19, Page 73) pertaining to easily soluble nature of hemimorphite and willemite is

supported by leaching and X-ray work done by us on enriched zinc silicate ores (Fig.18, Table 15). Low recovery of zinc in ordinary acid leaching of slag may be explained in terms of formation of colloidal silica and subsequent occlusion/adsorption (Ref.19, Page 73; Ref.26, Page^c136). Another factor responsible for low recovery of zinc could be poor grade of slag, poor liberation and accessibility of zinc containing phases.

Heating of slag to high temperature results in decomposition of some phases on the one hand and formation of difficultly soluble zinc ferrite phases on the other (Table 4).

Low recovery of zinc in sulfuric acid leaching is usually explained in terms of the adsorption properties of colloidal silica as mentioned earlier. Leaching of silicate phases willemite ($2 \text{ ZnO} \cdot \text{SiO}_2$) and hemimorphite ($\text{Zn}_4\text{Si}_2\text{O}_7(\text{OH})_2\text{H}_2\text{O}$) results in the formation of monomeric and dimeric silicic acid along with zinc sulfate (Ref.19, Page 73). These silicic acid polymerizes with time and attains colloidal dimensions (Ref.19, Page 73). The extent of polymerization is^a function of time, temperature, pH and concentration (Ref.28, Page 175). Increase in time, temperature and pH enhance polymerization (Ref.28, Page 175). However, as Ashdown et al. (Ref.30, Page 7) point out that soluble silica (mainly monosilicic acid) is quite stable at pH 2 or below. Soluble silica can easily be precipitated in pH range 40-50 without forming a poorly filterable or unfilterable gel, where all or much of the zinc is occluded (Ref.26, Page 136;

Ref.19, Page 74). Shergold and Kesler (Ref.26, Page 136) hint that monosilicic acid also forms an unfilterable gel or poorly filterable precipitate. Other workers (Ref.19, Page 76; Ref. 30, Page 7) however feel, that monosilicic acid can be easily precipitated and filtered.

In the light of above discussions, decrease in recovery of zinc in sulfuric acid leaching with increasing temperature (Fig.12(a)) is expected. Since higher temperature enhances polymerization. We have found the maximum recovery of zinc in ordinary sulfuric acid leaching approximately of the order of 50%, i.e., 50 pct. zinc remains unrecovered. Apart from colloidal silica other factors which might be responsible for low recovery are presence of free silica and grade of slag.

Miller (Ref.28, Page 505) points out that residual valences of siloxane (Si-O-Si) surface of SiO_2 react with water such that surface becomes covered with silanol (SiOH) group. There is literature available (Ref.28, Page 672) which suggest that metal ions are adsorbed on hydroxylated silica surface.

For zinc silicate ores Mathew and Elsner (Ref.19, Page 76) point out that recovery value goes down as the grade of ore decreases. In case of ancient slag we feel this may be true because what we have is mostly gangue material.

As pointed out earlier ^(Ref.28, p. 175) increase in temperature increases polymerization so at low temperature we are expected to have more soluble silica and less of colloidal silica,

whereas reverse should be true at higher temperature. Conventional sulfuric acid leaching when coupled with neutralisation step shows improved recovery for ancient slags (Fig.12(b)). When neutralisation is done soluble silica is precipitated in easily filterable form, (Ref.30, Page 7) and removed easily. Hence recovery is high at low temperature.

The unique position of Al^{3+} ions with regard to silicic acid and silica is well known. Al^{3+} plays a dual role:

- it decreases the solubility of silica (Ref.28, Page 56)
- colloidal silica can be precipitated most effectively in pH range 4-5. This is because below pH 4 the charge on silica is too small and above pH 5 charge is quite large, so large amount of Al^{3+} ions is required (Ref.28, Page 81) Al^{3+} ions combines with soluble silica in pH range 5-9 (Ref.28, Page 81).

The adsorption of various ions on silica surface and colloidal silica have been studied (Ref. 28, Page 672). It has been pointed out that Al^{3+} ions adsorbs more preferentially than other ions such Fe^{3+} and Zn^{2+} (Ref. 28, Page 672) (Ref. 28, Page 183).

Since the fraction of colloidal silica increases with increasing temperature and Al^{3+} ions can handle only colloidal silica at low pH (5.0) and not soluble silica (Ref.28, Page 81), the effectiveness of Al^{3+} addition at higher temperature and pH can explain higher zinc recovery at higher temperature (Fig.12(c) and 12(d)).

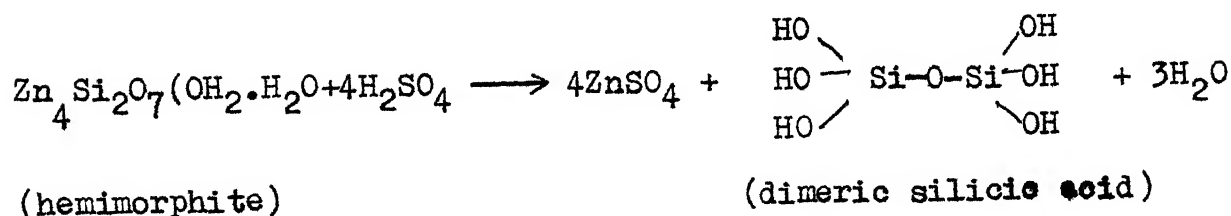
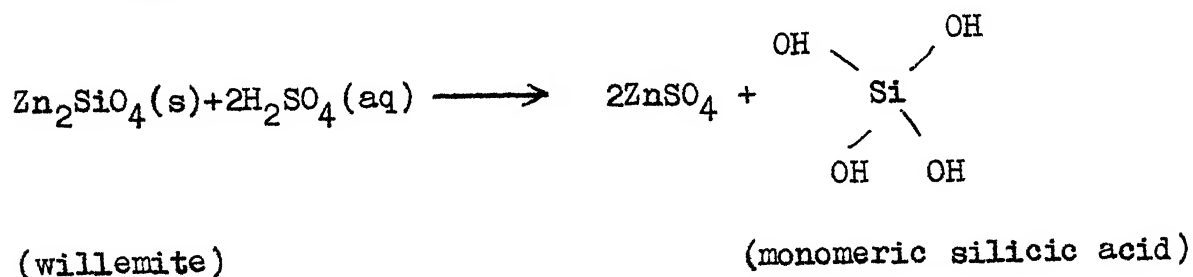
pH vs. recovery plot for modified sulfuric acid leaching of ancient slag at 90°C shows a maxima at pH approximately 4.5 (Fig.13(d)). This maxima corresponds to the most effective pH for precipitating aluminium-silica complex (Ref. 28, Page 673). Upto pH 5.5, pH seems to have no effect in modified sulfuric acid leaching at 50°C (Fig.13(c)). This is probably due to the fact that soluble silica is effectively precipitated at higher pH. Percentage zinc recovered vs. pH plots (Fig.13(a) and 13(b)) also shows a maxima at pH approximately 4.5. This matches with the result of other workers (Ref.33), (Ref.30, Page 7).

In case of fast leaching most important parameter is water slag ratio provided sufficient acid is present (Ref.37, Page 9). The decrease of zinc recovery for ancient slag with increasing water slag ratio (Fig.14) can be explained on the basis of ^{the} fact (Ref. 37, Page 9) when amount of water increases more and more water is available for hydration of silica. Increase in hydration result in problem like poor filtration and occlusion of zinc (Ref. 37, Page 10). Increase in acid slag ratio increases zinc recovery (Fig.15) for the same water slag ratio, this probably is concentrations effect.

The change in temperature of slurry leach mass with time is shown in (Table 14). Little effect of aging temperature and time (Fig.16, and Fig.17) on zinc recovery is due to fact when temperature of aging is 50-60°C the temperature by slurry leach mass is significantly higher (Table 14).

The results of chemical analysis and X-ray (Table 15) for enriched ore samples containing hemimorphite and willemite shows that these phases are easily soluble. Similar results have been reported by Mathew and Elsner (Ref.18 and 19).

In the case of hemimorphite, neutralisation seems to have some effect on zinc recovery. This can be ^{explained} with the help of following reactions:



It is presumed that only polysilicic acid lowers zinc recovery (Ref.19, Page 73,74) and hence zinc recovery problem may be faced acutely in the case of hemimorphite. Neutralisation and use of Al^{3+} ions improves zinc recovery. This is justified by the data obtained by us. (Table 15)

Final Recommendations

Both fast leaching and acid leaching show comparable recovery of zinc approximately 80 and 85% respectively. The number of steps involved are less in fast leaching for which we do not require any neutralizing agent and aluminium sulfate.

However, filterability in case of acid leaching is much superior as compared to fast leaching. We feel that if a two step neutralisation is coupled with fast leaching it might show better result.

In the first step of neutralisation (upto pH 2) roasted zinc sulphide ore can be used and in the second step (upto pH 4.5) cheap neutralising agent such as lime stone can be used. The purpose of having two step neutralisation is the following: as the pH is raised beyond 2 the rate of dissolution of calcined ore decreases and iron contamination increases. The second step of neutralisation should therefore be done by some cheap neutralising agent.

The concentration of zinc in the leach solution obtained after leaching of slag is quite low (≈ 2.0 g/l). When compared with the typical analysis of neutral overflow in zinc industry as shown below (45),

Element	Concentration in Neutral overflow
Zn	130 g/L
Ni	2.0 mg/l
Co	7.6 mg/l
Cu	240.0 mg/l
Cd	900 mg/l
Fe (total)	3.0 mg/l
Fe (sol)	0.2 mg/l
As (sol)	Traces
Ge (sol)	0.111 mg/l

we see that zinc concentration in actual practice is 50-75 times more than the zinc in slag leach solution. Two things are clear from this (i) a separate plant is not possible for ancient slag (ii) zinc concentration of the leach solution should be upgraded, if it is to be used for electrolysis.

There are various possibilities which can be tried for upgrading Zinc content of the leach solution obtained after slag leaching. There is a possibility that leach solution can be used as a substitute for water in leaching unit of zinc industry.

As is well known, that during electrowinning of Zinc, there is an increase in sulfuric acid concentration and significant zinc remains in solution after electrolysis, the acid obtained from electrolytic cell if used in leaching of slag, is expected to upgrade the Zinc concentration of leach solution.

As suggested earlier use of calcine ore as neutralising agent will also upgrade the Zinc concentration.

The purification of upgraded solution may be done with the usual methods employed in Zinc industry.

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APPENDIX A

The operating characteristics of the instrument used for atomic adsorption spectrophotometry are as follows:

Light source	Hollow cathode
Lamp current	3 mA
Wave length	213.9 nm
Slit width	320 m
Burner head	Single slot
Flame description	Air-acetylene oxidizing fuel, lean, blue
Range	Linear upto a concentration of approximately 1 g/ml (1 ppm)

Standard solution of zinc was prepared as per instruction given in the operation mannual of the instrument. 1.0 gm zinc metal was dissolved in 50 ml, HCl (1:1) and final volume was made upto 1000 ml. This gave solution containing 1000 ppm Zn. Aliquots of 0.2, 0.4, 0.6 and 0.8 ml were taken from the standard solution of zinc and diluted to 100 ml which corresponded to 0.2, 0.4, 0.6 and 0.8 ppm of zinc, rexpectively. The calibration curve is shown in Fig.19.

In order to ascertain whether there was any interference due to Fe^{++} , Fe^{+++} , Cd^{++} , Ca^{++} or Mg^{++} , a known concentration zinc solution (0.4 ppm) was taken with varying concentrations of FeSO_4 , $\text{Fe}_2(\text{SO}_4)_3$, CaSO_4 , MgSO_4 , CdSO_4 and zinc was estimated using the atomic absorption spectrophotometry.

It is evident from the following table.

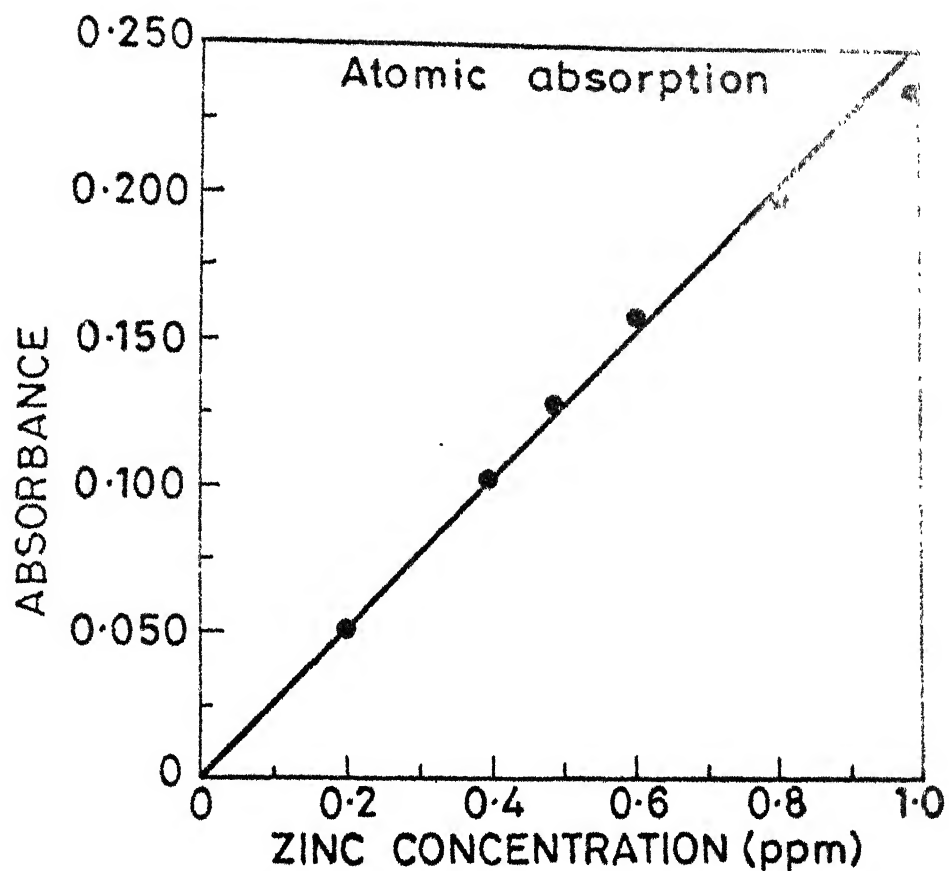


FIG. 19. CALIBRATION CURVE FOR ZINC.

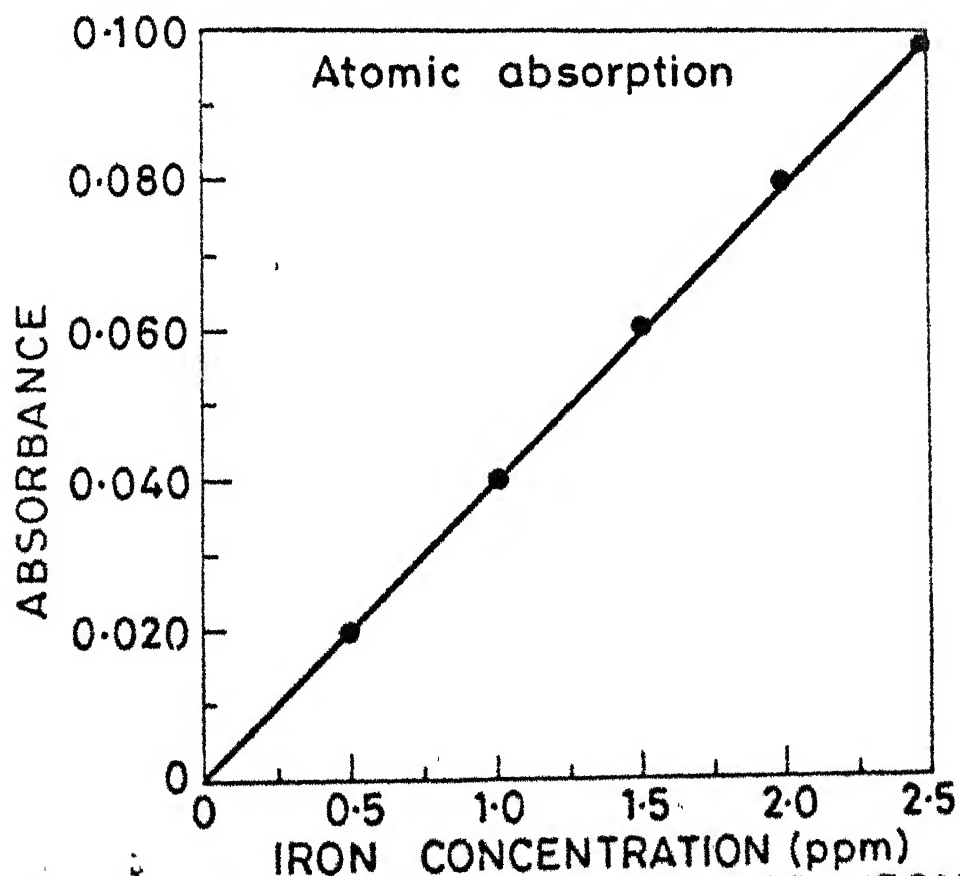


FIG. 20. CALIBRATION CURVE FOR IRON

Concentration	Zinc Concentration (ppm)
1 ppm FeSO_4 + 0.4 ppm zinc	0.384 ± 0.017
2 ppm FeSO_4 + 0.4 ppm zinc	0.388 ± 0.018
4 ppm FeSO_4 + 0.2 ppm zinc	0.370 ± 0.024
1 ppm $\text{Fe}_2(\text{SO}_4)_3$ + 0.4 ppm zinc	0.374 ± 0.034
2 ppm $\text{Fe}_2(\text{SO}_4)_3$ + 0.4 ppm zinc	0.377 ± 0.016
3 ppm $\text{Fe}_2(\text{SO}_4)_3$ + 0.4 ppm zinc	0.363 ± 0.021
4 ppm $\text{Fe}_2(\text{SO}_4)_3$ + 0.4 ppm zinc	0.381 ± 0.027
1 ppm CaSO_4 + 0.4 ppm zinc	0.401 ± 0.006
1.5 ppm CaSO_4 + 0.4 ppm zinc	0.418 ± 0.015
2.0 ppm CaSO_4 + 0.4 ppm zinc	0.409 ± 0.011
0.5 ppm CdSO_4 + 0.4 ppm zinc	0.409 ± 0.015
1.0 ppm CdSO_4 + 0.4 ppm zinc	0.394 ± 0.022
1.5 ppm CdSO_4 + 0.4 ppm zinc	0.414 ± 0.026
0.1 ppm MgSO_4 + 0.4 ppm zinc	0.403 ± 0.010
0.2 ppm MgSO_4 + 0.4 ppm zinc	0.398 ± 0.026
0.3 ppm MgSO_4 + 0.4 ppm zinc	0.382 ± 0.010
0.1 ppm $\text{Al}_2(\text{SO}_4)_3$ + 0.4 ppm zinc	0.396 ± 0.007
0.2 ppm $\text{Al}_2(\text{SO}_4)_3$ + 0.4 ppm zinc	0.386 ± 0.006
0.3 ppm $\text{Al}_2(\text{SO}_4)_3$ + 0.4 ppm zinc	0.386 ± 0.006

that there was no significant interference in the air-acetylene flame due to presence of Fe^{++} , Fe^{+++} , Cd^{++} , Ca^{++} , Mg^{++} or Al^{3+} .

Standard for Fe was prepared by a method similar to Zn.

Calibration curve is shown in Fig.20.

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